



Environment

Submitted to:  
Sumitomo Metal Mining Pogo LLC  
Delta Junction, Alaska

Submitted by:  
AECOM  
Fort Collins, Colorado  
60284905.1100  
May 2013

# Sumitomo Metal Mining Pogo LLC CISWI Test Plan



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A handwritten signature in black ink, appearing to read "Doug Bopray".

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Prepared By: Doug Bopray  
Air Quality Scientist

A handwritten signature in black ink, appearing to read "John S. Rosburg".

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Reviewed By: John Rosburg  
Emissions Measurements Manager

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## 1.0 Introduction

Sumitomo Metal Mining Pogo LLC (Pogo) mine facility is located near Delta Junction, Alaska 99737. The Pogo facility operates under the Alaska Department of Environmental Conservation (ADEC), Air Quality Control Minor Permit Number AQ0406MSS05, issued on May 12, 2011. In the operation of the facility, Pogo employs Unit 412 which is an incinerator used to burn facility waste. This test program is designed to evaluate Unit 412 pollutant emission rates with regard to the Commercial and Industrial Waste Incinerator (CISWI) emission limits. The test program will serve as an initial performance test to demonstrate compliance with the CISWI emission standards, and to determine what, if any, pollution controls are needed to achieve compliance. The field measurements of Unit 412 include the following:

- Particulate (PM);
- Nitrogen Oxides (NO<sub>x</sub>);
- Dioxins and Furans (D/F);
- Cadmium (Cd);
- Mercury (Hg);
- Sulfur Dioxide (SO<sub>2</sub>);
- Carbon Monoxide (CO);
- Hydrochloric Acid (HCl); and
- Lead (Pb).

The measurements and analytical procedures to be followed for this test project are accepted United States Environmental Protection Agency (USEPA) Reference Method (RM) procedures and defined in the Code of Federal Regulations, Title 40, Part 60 (40 CFR 60), Appendix A. The measurements results will be provided in the same engineering units as the applicable emissions standards and will be directly compared to the established standards.

Pogo has retained AECOM, Technical Services, Inc. (AECOM) to perform the required emissions measurements. AECOM is located at 1601 Prospect Parkway, Fort Collins, Colorado 80525-9769. Mr. John Rosburg, AECOM Emissions Measurements Manager, is the Project Manager for this test program. Mr. Rosburg may be reached by telephone at (970) 219-4904 or by e-mail at john.rosburg@aecom.com. Ms. Sally McLeod of Pogo will be responsible for the coordination of the test program and collection of process data. Ms. McLeod may be reached by telephone at (907) 895-2879, by cell phone at (907) 978-3774, or by e-mail at Sally.Mcleod@smpmogo.com.

The following test plan is organized as follows: the testing approach is provided in Chapter 2.0; a description of the process is provided in Chapter 3.0; source test methodology, calculations, and nomenclature are presented in Chapter 4.0; a concise description of the quality assurance/quality control (QA/QC) procedures to be implemented is provided in Chapter 5.0; copies of the field data sheets to be used are provided in **Appendix A**; and copies of the source test methods are provided in **Appendix B**.

## 2.0 Test Approach

This test plan and protocol outlines specific methods and procedures for quantifying average PM, SO<sub>2</sub>, NO<sub>x</sub>, CO, D/F, HCl, Cd, Pb, and Hg emissions results from the Unit 412. All measurements and procedures are accepted United States Environmental Protection Agency (USEPA) Reference Method (RM) procedures and are defined in the Code of Federal Regulations, Title 40, Part 60 (40 CFR 60), Appendix A. **Table 2-1** provides the test matrix for the source to be tested and includes the test parameter, methods to be followed, number of sample runs and run duration. The test matrix shown in **Table 2-1** is based on the performance test requirements of the CISWI rule for small remote incinerators (see 40 CFR 60 Subpart CCCC, Table 8) The results of the field measurements results will be directly compared to the CISWI emission standards to evaluate compliance status and determine if pollution control is necessary.

**Table 2-1 Unit 412 Test Matrix**  
**Sumitomo Metal Mining Pogo LLC**

Source ID	Test Type	Test Parameter	Method	Number of Runs	Minimum Sample Volume	Minimum Run Duration
Incinerator	Performance Test	Sample Points	RM 1	1	NA	NA
		Velocity	RM 2	3	NA	60 min
		Molecular Weight (O <sub>2</sub> & CO <sub>2</sub> )	RM 3A	3	NA	NA
		Moisture	RM 4	3	21 dscf/run	60 min
		Particulate	RM 5	3	1 dscm/run	60 min
		Sulfur Dioxide	RM 6C	3	NA	60 min
		Nitrogen Oxides	RM 7E	3	NA	60 min
		Carbon Monoxide	RM 10	3	NA	60 min
		Dioxin/Furan	RM 23	3	1 dscm/run	120 min
		Hydrochloric Acid	RM 26A	3	1 dscm/run	60 min
		Metals (Cd, Pb, Hg)	RM 29	3	2 dscm/run	120 min

Pogo must submit the test plan to the ADEC in accordance with the timeline specified in ADEC, Air Quality Control Minor Permit Number AQ0406MSS05, Condition 26. Condition 26 states that before conducting any source test, the Permittee shall submit a plan to the Department. The plan must include the methods and procedures to be used for sampling, testing and quality assurance and must specify how the source will operate during the test and how the Permittee will document that operation. The Permittee shall submit a complete plan within 60 days after receiving a request under Condition 24 and at least 30 days before the scheduled date of any test unless the Department agrees in writing to some other time period. Further, at least 10 days before conducting a source test, the Permittee shall give the Department written notice of the date and the time the source test will begin.

This test plan includes a description of the test methods, duration of sample runs, test locations, and source operations during testing. No deviations from the selected methodologies are anticipated.

### 2.1 Schedule

AECOM has scheduled the field program to be conducted on approximately June 28, 2013. On Day 1 of the field effort, AECOM will prepare the equipment for testing. Day 2 will entail the performance of one combined PM and HCl sample run, one metals (Cd, Pb, Hg) sample run, one D/F sample run and one combined NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>2</sub> and CO<sub>2</sub> sample run. On Day 3 one combined PM and HCl sample run, one metals (Cd, Pb, Hg) sample run, one D/F sample run and one combined NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>2</sub> and CO<sub>2</sub>

sample run will be conducted. Day 4 entail the performance of one combined PM and HCl sample run, one metals (Cd, Pb, Hg) sample run, one D/F sample run and one combined NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>2</sub> and CO<sub>2</sub> sample run. Day 5 will allow for sample runs to be performed if the schedule is not maintained. Demobilization of the equipment and sample shipping will also be conducted on Day 5.

Per Condition 27 of the permit, Pogo will submit a test notification letter at least 10 days prior to conducting this source test project to the ADEC. The test notification letter will define the mutually agreed upon scheduled test dates. If an unforeseen issue requires the test dates to be altered, the ADEC will be notified as soon as practicable to discuss alternatives.

## **2.2 Equipment Preparation**

All equipment will be prepared and calibrated in accordance with USEPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III; Stationary Source Specific Methods, 40 CFR 60, Appendix A; and AECOM's general QA/QC policy described in Chapter 5.0 of this protocol. These procedures meet or exceed all USEPA requirements and guidelines for equipment maintenance and calibration. All equipment will be in proper working order prior to mobilization to the facility.

## **2.3 Field Measurements**

The Unit 412 incinerator test program will be performed approved USEPA methods. The methods selected and listed in Table 2-1 above are applicable for the determination of the pollutant parameters required by the CISWI Rule. The PM/HCl, metals (Cd, Pb, Hg) and D/F samples will be withdrawn isokinetically from the source and collected on the front-half and condensate portions of the sample train. The sample volume collected during each run are specific to the pollutant parameter and dictated by the CISWI Rule. A total of three, with a minimum sample run time of one hour, sample runs will be performed for combined PM/HCl. A total of three, with a minimum sample run time of two hours, sample runs will be performed for metals (Cd, Pb, Hg). A total of three, with a minimum sample run time of four hours, sample runs will be performed for D/F.

The gaseous pollutant (SO<sub>2</sub>, NO<sub>x</sub>, CO) and diluents (O<sub>2</sub> and CO<sub>2</sub>) parameters will be measured with a continuous emission monitor system (CEMS). A minimum of three, one hour, sample runs will be performed. The response of the instruments in the CEMS will be digitally recorded, at one minute intervals, using Campbell Data Acquisition System (DAS). The CEMS will be calibrated with certified Protocol 1 calibration gas standards.

## **2.4 Final Test Report**

The Final Report will contain the following sections at a minimum:

- Executive Summary
- Introduction
- Summary of Results
- Source Description and Operation
- Sampling Methodology
- QA/QC Procedures
- Appendices

The Appendices will contain equipment calibration, field data sheets, calculations, and any other pertinent data such as process information. The final report will be published and provided to the ADEC no later than 60 calendar days from the completion of the field program.

## 3.0 Process Description and Operation

### 3.1 Process Description

Unit 412 is an ACS, Inc., Model CA 400, industrial waste incinerator used to reduce the amount of waste transported off site from the Pogo facility. The unit is fired by propane. The capacities of the unit are as follows:

- Rated Capacity of 240 Lb/hr - Type '0' Waste;
- Rated Capacity of 400 Lb/hr - Type '1' Waste;
- Rated Capacity of 480 Lb/hr - Type '2' Municipal Solid Waste;
- Rated Capacity of 240 Lb/hr - Type '3' Waste;
- Rated Capacity of 200 Lb/hr - Type '4' Pathological Waste; and

### 3.2 Process Operation

The emission measurements of Unit 412 will be conducted under normal and representative process operations at the maximum achievable waste burning rate at the time of testing. For all measurements associated with Unit 412, all pertinent process and control device operations data will be monitored and recorded. The following parameters will be monitored and recorded during each sample run;

- Weight of each batch loaded into the incinerator;
- Time interval between batches loaded;
- Primary oven temperature at 30-minute intervals;
- Secondary oven temperature at 30-minute intervals;
- Primary oven burn time following loading of final batch; and
- Secondary burn time following completion of the primary burn cycle.

Process operations data for the time periods during which testing is conducted will be provided in final test report.

## 4.0 Methodology

The testing program will be performed according to the following accepted and approved USEPA RMs as contained in the USEPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods, 40 CFR 60, Appendix A. The general procedures that will be followed for this measurements evaluation include:

- RM 1 – Sample Velocity Traverse for Stationary Sources;
- RM 2 – Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube);
- RM 3A – Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure);
- RM 4 – Determination of Moisture Content In Stack Gases;
- RM 5 – Determination of Particulate Matter Emissions from Stationary Sources;
- RM 6C – Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure);
- RM 7E – Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure);
- RM 10 – Determination of Carbon Monoxide Emissions from Stationary Sources;
- RM 023 – Determination of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Emissions from Municipal Waste Combustors;
- RM 26A – Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method; and
- RM 29 – Determination of Metals Emissions from Stationary Sources.

### 4.1 Support Measurements for Stack Parameters

USEPA RMs 1 through 4 will be performed in support of the emissions measurements procedures selected for quantifying pollutant emission rates. RM 1, selection of sample points for velocity and particulate traverses, will be conducted prior to the initiation of any emission measurements at test location. The determination of stack gas flow rate, molecular weight, and moisture content (RMs 2 through 4) will be integrated into and performed concurrently with each RM 29 sample run.

#### 4.1.1 Selection of Traverse Points by Reference Method 1

USEPA RM 1, "Sample Velocity Traverses for Stationary Sources," will be followed for the selection of measurement points at the test location. The physical characteristics of the test location meet the minimum criteria of RM 1 for isokinetic sampling. The calculated measurement points will be used for all isokinetic sample runs.

#### 4.1.2 Flow Rate Determination by Reference Method 2

USEPA RM 2, "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube)," will be followed to measure the volumetric flow rate during each sample run at the sample location. This method will be incorporated into, and conducted concurrently with, each isokinetic sample run.

RM 2 allows for a stainless steel Type-S or standard pitot tube to be connected to a differential pressure gauge (inclined manometer). The measured pressure differential, observed at each traverse point, will be recorded on field data forms and used in determining the overall emission rate for each constituent.

In addition to velocity pressures, gas temperatures will be measured and recorded concurrently with all differential pressure data. The temperature will be measured with a Type K thermocouple located at the measurement tip of the pitot tube (in the same measurement plane). The Type K thermocouple will be connected directly to a calibrated digital temperature indicator for accurate measurements.

#### **4.1.3 Molecular Weight Determination by Reference Method 3**

USEPA RM 3A, "Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)," will be conducted concurrently with the pollutant measurements at the test location. Sample gas will be continuously extracted from the Unit 412 exhaust stack and directed to a combination O<sub>2</sub>/CO<sub>2</sub> analyzer. Diluent O<sub>2</sub> and CO<sub>2</sub> data collected during the course of the sampling will be used to determine effluent gas dry molecular weight in accordance with USEPA RM 3A. If isokinetic sampling is conducted without continuous O<sub>2</sub> and CO<sub>2</sub> analysis, an integrated Tedlar bag sample will be collected and subjected to the combination O<sub>2</sub>/CO<sub>2</sub> instrument for analysis. The results of the O<sub>2</sub> and CO<sub>2</sub> analysis will be used for the determination of effluent molecular weight.

USEPA RM 3A analyzer calibration requirements include; three point calibrations using USEPA Protocol 1 gas standards, and stringent instrument drift requirements. Calibrations will be completed at 80 to 100 percent of the full span value, 40 to 60 percent of the full span value, and 0 percent of the full span value (ultra-pure nitrogen for both analyzers).

The O<sub>2</sub>/CO<sub>2</sub> analyzer will be subjected to a zero and two up-scale calibration gases prior to and upon completion of the RATA sample runs. The gas standards will be certified and traceable to USEPA Protocol 1 specifications, which require that the gas concentration be within  $\pm 1$  percent of the documented value. The response of the analyzers compared to each certified calibration standard must be within  $\pm 2$  percent of the high calibration gas standard (CS) value for each component as required by the method.

To calibrate the instruments, the gas standards will be introduced directly to the monitors at the sample inlet located on the back of each instrument. For the continuous measurements, the amount of bias of the O<sub>2</sub>/CO<sub>2</sub> instrument will also be determined. This will be accomplished by introducing zero and one span gas to the instrument at the point at which the sample probe and heated sample filter are connected. The response of the analyzers to the direct zero and span gases (bias check) must be less than  $\pm 5$  percent of the span value for each component as required by the method. The bias calibration check will be performed prior to and upon completion of each RATA sample run.

The magnitude of calibration drift will be calculated. Calibration drift is the difference in the initial (pre-test) bias calibration response and the final (post-test) bias calibration response for the same gas standard. The calibration drift must be within  $\pm 3$  percent of the CS over each sample run for each O<sub>2</sub>/CO<sub>2</sub> gas standard as required by RM 3A.

USEPA RM 3A, "Gas Analysis for the Determination Dry Molecular Weight," will be conducted for all mercury sample runs. Effluent sample gas will be extracted from each exhaust and collected in a clean dry tedlar bag. Each bag sample will be subjected to an Orsat or Fyrite for analyses of oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). Diluent O<sub>2</sub> and CO<sub>2</sub> analyses results will be used to calculate the effluent gas dry molecular weight.

#### **4.1.4 Percent Moisture Determination by Reference Method 4**

USEPA RM 4, "Determination of Moisture Content in Stack Gases," will be incorporated into each mercury sample run. The determination of moisture content will be accomplished by using a condenser and pump assembly, connected between a sample probe and metering system and performed concurrently with each RM 29 sample run.

Throughout each isokinetic sample run, a known volume of gas (measured by a dry gas meter) will be passed through the condenser assembly. Upon completion of each sample run, the total amount of condensate collected will be gravimetrically measured and the net gain calculated. The total moisture gain, volume of gas extracted, and measured meter temperature data will be used to calculate the actual moisture content of the effluent.

#### **4.2 Particulate Determination by Reference Method 5**

USEPA RM 5, "Determination of Particulate Matter Emissions from Stationary Sources" will be followed to determine particulate emission rates. Each RM 5 will be conducted in accordance with all applicable USEPA quality assurance requirements

Samples will be withdrawn isokinetically (100 percent  $\pm$  10 percent) from the source using a modular isokinetic sampling system. The sampling train will consist of a stainless steel nozzle, heated stainless steel probe with an S-Type pitot tube attached, a heated filter, four chilled impingers, and a metering console. The particulate sample will be collected on a quartz fiber filter supported by a Teflon frit and maintained at a temperature of  $248 \pm 25^{\circ}\text{F}$ . The impinger train will be consistent with RM 5.

The system vacuum will extract the effluent gas through the interconnected, leak-free components. The entire system will be "leak checked" before and after each individual sample run to ensure sample integrity following RM 5 procedures.

A "K-factor" (coefficient) will be determined prior to the initiation of each sample run. This coefficient will be based upon preliminary measurements of gas temperature, flow rate, pressure, and moisture content. Multiplying the K-factor by the measured differential pressure will determine the isokinetic sample rate for each sample point. If a variable changes during a sample run, the coefficient will be adjusted to maintain isokinetic sampling rates. At isokinetic conditions, the velocity of the stack gas entering the nozzle of the extraction system will be equal to the effluent velocity at the sample point.

The quartz filter will be removed from the filter holder and placed in a Petri dish and sealed. The impingers will be recovered following RM 5 procedures. The RM 5 sample recovery will be conducted in accordance with all applicable USEPA quality assurance requirements.

#### **4.3 Sulfur Dioxide Determination by Reference Method 6C**

Sulfur dioxide emissions will be quantified at the Unit 412 exhaust stack according to USEPA RM 6C, "Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)." This method allows for the determination of  $\text{SO}_2$  concentrations by continuously extracting stack effluent and directing a portion of the sample to an  $\text{SO}_2$  analyzer. An AMETEK Model 921M UV photometric  $\text{SO}_2$  monitor will be used to measure the concentration (parts per million [ppm] by volume) of the effluent at the test location on a dry basis.

RM 6C provides rigorous analyzer calibration requirements, including three point calibrations using USEPA Protocol 1 gas standards, and stringent instrument drift requirements. Calibrations will be performed at 80 to 100 percent of the span value, 40 to 60 percent of the span value, and 0 percent of the span value (ultra-pure nitrogen).

The  $\text{SO}_2$  analyzer will be subjected to the zero and two up-scale calibration gases prior to and upon completion of the test series. The gas standards will be certified and traceable to USEPA Protocol 1 specifications, which require that the gas concentration be within  $\pm 1$  percent of the documented value. The response of the analyzer compared to each certified calibration standard must be within  $\pm 2$  percent of the CS value for each component. To calibrate the instrument, the gas standards will be introduced to the inlet of the  $\text{SO}_2$  RM analyzer before and upon completion of each test series. The amount of bias of the  $\text{SO}_2$  RM system also will be determined before and after each sample run. This will be accomplished

by delivering zero and one span gas directly to the point where the sample probe and heated sample filter are connected. The response of the analyzer to the bias checks must be less than  $\pm 5$  percent of the span value for each check.

The magnitude of calibration drift also will be calculated. Calibration drift is the difference in the initial bias calibration response check and the final bias calibration response check for the same gas standard. The calibration drift must be within  $\pm 3$  percent of the span for each sample run.

#### **4.4 Nitrogen Oxides Determination by Reference Method 7E**

USEPA RM 7E, "Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)," will be used to accomplish the Unit 412 NO<sub>x</sub> measurements. This method allows for the determination of NO<sub>x</sub> concentrations by continuously extracting effluent from the stack and directing a portion of the sample to a NO<sub>x</sub> analyzer. A TEI Model 42C Chemiluminescent NO<sub>x</sub> analyzer will be used to measure the concentration (ppm by volume) of the effluent at the stack on a dry basis.

USEPA RM 7E provides rigorous analyzer calibration requirements, including three point calibrations using EPA Protocol 1 gas standards, and stringent instrument drift requirements. Calibrations will be completed at 80 to 100 percent of the span value, 40 to 60 percent of the span value, and zero percent of the span value (ultra-pure nitrogen).

The NO<sub>x</sub> analyzer will be subjected to a zero and two up-scale calibration gases prior to the performance of the sample runs. The gas standards will be certified and traceable to USEPA Protocol 1 specifications, which require that the gas concentration is within  $\pm 1$  percent of the documented value. The response of the analyzer compared to each certified calibration standard must be within  $\pm 2$  percent of the CS for each component.

To calibrate the instrument, the gas standards will be introduced directly to the NO<sub>x</sub> monitor at the sample inlet located on the back of the instrument. The amount of bias of the NO<sub>x</sub> CEM system also will be determined. This will be accomplished by introducing zero and one span gas to the NO<sub>x</sub> system at the point in which the sample probe and heated sample filter are connected. The response of the analyzer system to the zero and span gas (bias check) must be less than  $\pm 5$  percent of the CS for each component. The bias calibration check will be performed prior to, and upon completion of, each sample run.

The magnitude of calibration drift will also be calculated. Calibration drift is the difference in the initial (pre test) bias calibration response and the final (post test) bias calibration response for the same gas standard. The calibration drift must be within  $\pm 3$  percent of the CS each sample run for each gas standard.

#### **4.5 Carbon Monoxide Determination by Reference Method 10**

The CO measurements will be conducted according to USEPA RM 10, "Determination of Carbon Monoxide Emissions from Stationary Sources." Sample gas will be continuously extracted from the test location and directed to a TEI Model 48C, Gas Filter Correlation (GFC), NDIR CO instrument for analysis. The GFC feature of the CO analyzer eliminates potential interference by substances, which absorb infrared energy.

USEPA RM 10 provides rigorous analyzer calibration requirements, including three point calibrations using EPA Protocol 1 gas standards, and stringent instrument drift requirements. Calibrations will be completed at 80 to 100 percent of the span value, 40 to 60 percent of the span value, and zero percent of the span value (ultra-pure nitrogen).

The CO analyzer will be subjected to a zero and two up-scale calibration gases prior to the performance of the sample runs. The gas standards will be certified and traceable to USEPA Protocol 1 specifications, which require that the gas concentration is within  $\pm 1$  percent of the documented value. The response of the analyzer compared to each certified calibration standard must be within  $\pm 2$  percent of the CS for each component.

To calibrate the instrument, the gas standards will be introduced directly to the CO monitor at the sample inlet located on the back of the instrument. The amount of bias of the CO CEM system also will be determined. This will be accomplished by introducing zero and one span gas to the CO system at the point in which the sample probe and heated sample filter are connected. The response of the analyzer system to the zero and span gas (bias check) must be less than  $\pm 5$  percent of the CS for each component. The bias calibration check will be performed prior to, and upon completion of, each sample run.

The magnitude of calibration drift will also be calculated. Calibration drift is the difference in the initial (pre-test) bias calibration response and the final (post test) bias calibration response for the same gas standard. The calibration drift must be within  $\pm 3$  percent of the CS each sample run for each gas standard.

#### **4.6 Dioxins and Furans Determination by Reference Method 23**

USEPA RM 23, "Determination of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Emissions from Municipal Waste Combustors," will be followed to determine D/F concentrations and emissions from the Unit 412 test location.

##### **4.6.1 Sample Train Component Preparation**

All glass parts of the sample train including the sorbent trap will be pre-cleaned prior to sampling according to the following procedures.

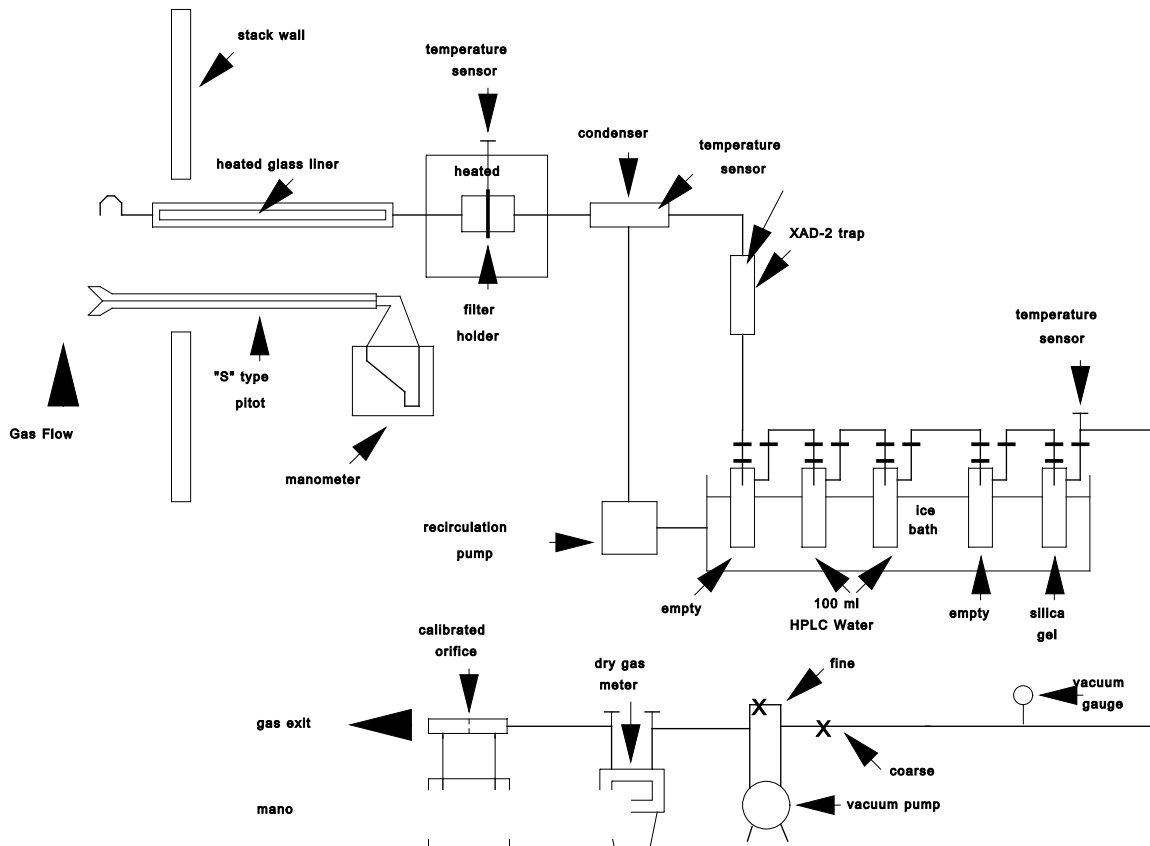
- Soak in hot soapy water (Alconox) at 50°C or higher;
- Rinse three times with tap water;
- Rinse three times with deionized water;
- Rinse three times with pesticide grade acetone;
- Rinse three times with pesticide grade methanol/methylene chloride;
- Bake at 450°F for 2 hours; and
- Seal with clean Teflon tape.

The glassware will be sealed with Teflon tape followed by aluminum foil until sample train assembly. Following sample recovery, the glassware will be reused at the same sampling location as allowed by the method.

The XAD-2 resin traps will be pre-cleaned and prepared by Analytical Perspectives. Each sorbent trap will be charged with 20 to 30 grams of the precleaned resin and the five surrogate compounds listed in Table 2 of RM 23 will be added to the resin. Care will be taken to ensure that the resin is kept at temperatures below 120°F during shipment and before and after sample collection to prevent resin decomposition. The time between charging the trap and use in the field will be minimized and will not be allowed to exceed 14 days. The sorbent traps will be shipped from Analytical Perspectives to AECOM's Fort Collins facility under strict chain-of-custody (COC) documentation.

#### 4.6.2 Sample Collection

Samples for D/F will be withdrawn isokinetically from the source using an RM 23 sampling train as depicted in **Figure 4-1**. The sampling train will consist of a Teflon coated stainless steel nozzle, a heated Teflon lined probe, a pretreated glass fiber filter maintained at a temperature of  $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$ , a water-cooled condenser, a sorbent trap containing XAD-2 resin, five chilled impingers, and a metering console. The water-cooled condenser and sorbent trap will be arranged in a manner that allows the condensate to drain vertically through the trap. Gas entering the trap will be maintained at or below  $68^{\circ}\text{F}$ . The first impinger (optional knockout) will be empty, the second and third impingers each will contain 100 ml of HPLC water, the fourth will be empty, and the fifth will contain pre-weighed silica gel. Sealing greases will not be used on any portion of the sample train.



**Figure 4-1 Reference Method 23 Sampling Train**

#### 4.6.3 Sample Recovery

Recovery of the samples and assembly of the sample trains for reuse will be conducted in a dust-free environment. Each impinger and the XAD-2 trap will be weighed prior to and at the conclusion of each sample run. The volume of water vapor condensed in the impingers, XAD resin and silica gel will be summed and entered into moisture content calculations.

All sample-exposed components of the sampling train will be rinsed with acetone and methylene chloride (rinses recovered per RM 23), and finally acetone (toluene rinse discarded per RM 23). Sample containers from a typical run include the following.

- Container 1 – Filter(s);
- Container 2 – Rinses of nozzle, probe, and front-half of filter holder and rinses of back-half of filter holder and condenser;
- Container 3 – XAD cartridge and resin;
- Container 4 – Impinger contents; and
- Container 5 – Silica gel.

The samples, comprised of containers 1 through 3, will be shipped to Analytical Perspectives, Inc. under strict COC documentation. Appropriate shipping containers will be used to keep the samples cool during shipping.

#### **4.6.4 Sample Analysis**

The RM 23A samples will be analyzed by Analytical Perspectives, Inc. in strict accordance with Analytical Perspective's QA Program. The filter(s), XAD-2 resin, toluene and methylene chloride rinses will be analyzed for tetra-octa (4-8) D/F according to USEPA RM 0023A with high-resolution gas chromatography/high resolution mass spectrometry. All extracts from one run will be analyzed in separate front half and back half sample fractions.

#### **4.6.5 Data Reduction**

The D/F results will be expressed in terms of toxicity equivalents (TEQ), as specified in 40 CFR §63.1342. The D/F congeners (tetra, hepta, hexa and octa) will be converted to TEQ using toxicity equivalence factors (TEFs), as the summation of the TEFs of the congeners, multiplied by their relative concentrations.

Any D/F congeners that are reported by Analytical Perspectives, Inc. as nondetected (below the method detection limit ND) shall be counted as zero for purposed of calculating the total D/F TEQ concentration for that sample, as specified in RM 0023A (§7.4).

#### **4.7 Hydrogen Chloride Determination by Reference Method 26A**

USEPA RM 26A, "Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method," will be followed for the determination of HCl emissions at the Unite 412 test location. This method will be performed in conjunction with the particulate measurement procedures as allowed by the methods. Included in the RM 26A sampling system will be a calibrated glass or Teflon coated nozzle, stainless steel probe, glass or Teflon probe liner, insulated filter oven, glass filter holder and tared quartz-fiber filter, condenser assembly, and calibrated extraction system. The system vacuum will extract the effluent sample gas through the interconnected, leak-free components. The entire system will be "leak checked" before and after each individual sample run to ensure sample integrity.

A "K-factor" (coefficient) will be determined prior to the initiation of each RM 26A sample run. This coefficient will be based upon preliminary measurements of gas temperature, flow rate, pressure, and moisture content. Multiplying the K-factor by the measured differential pressure at each sample point will provide for isokinetic sample rates for each sample point. If a variable changes during a sample run, the coefficient will be adjusted to maintain isokinetic sample rates. At isokinetic conditions, the velocity of the stack gas entering the nozzle of the extraction system will be equal to the effluent velocity at the sample point.

The condenser assembly will consist of a series of five glass impingers with glass inserts interconnected to each other by glass U-tubes, providing a "leak tight" seal with 28/15 ball and socket connections. The first and second impingers will contain sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The third and fourth impingers will contain sodium hydroxide ( $\text{NaOH}$ ). The fifth impinger will be filled with a pre-weighed amount of silica gel to capture any residual moisture from the sample stream. The impinger train will be set in an ice bath to maintain the extracted gas outlet temperature at or below 70°F. By cooling the sample, all water vapor and gases will be condensed and collected.

Three valid sample runs will be performed at the test location. Upon completion of each sample run, the probe will be removed from the effluent and allowed to cool. A leak check of the sampling system will then be performed to verify the integrity of the system. The leak rate must not exceed 0.02 actual cubic feet per minute (acfm) in order for the test to be considered valid.

Each sample train will be carefully recovered. The  $\text{H}_2\text{SO}_4$  solution in the first two impingers will be quantitatively recovered in a glass sample container. The impingers and connecting glassware will then be rinsed with water and added to the same sample jar. The contents of the third and fourth impingers will be placed in a glass sample jar. The silica gel from the fifth impinger will be weighed to determine the moisture gain.

Portions of the  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  absorbing reagents will be collected for blanks and diluted to the approximate volume of the corresponding sample jars with rinse water from the same wash bottle used. All liquid levels will be marked. The  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  sample jars and reagent blanks will be sent to TestAmerica located in West Sacramento, California for  $\text{HCl}$  and  $\text{Cl}_2$  analysis by IC.

#### **4.8 Metals Determination by Reference Method 29**

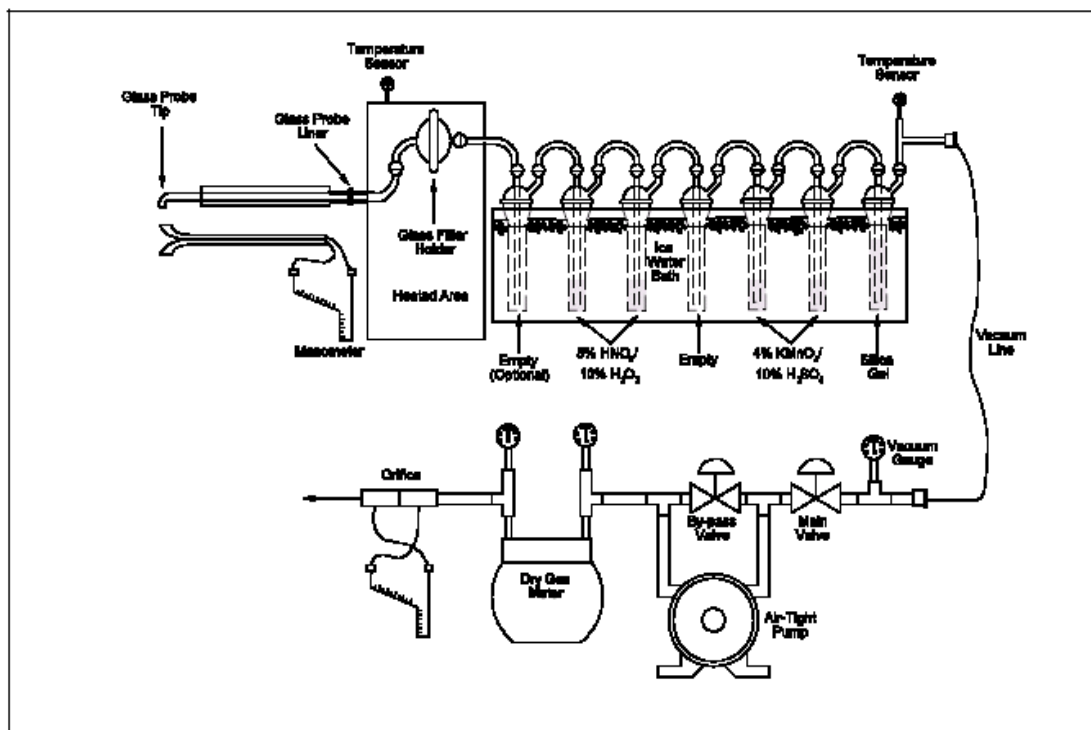
USEPA RM 29, "Determination of Metals Emissions from Stationary Sources," will be followed to determine the metals (Cd, Pb, Hg) emission rates exhausted by Unit 412. Included in the RM 29 sampling system will be a calibrated glass or Teflon coated stainless steel nozzle, stainless steel probe, glass or Teflon probe liner, insulated filter oven, glass filter holder and tared quartz-fiber filter, condenser assembly, and calibrated extraction system. The system vacuum will be used to extract the effluent gas through the interconnected, leak-free components. The entire system will be "leak checked" before and after each individual sample run to ensure sample integrity.

A "K-factor" (coefficient) will be determined prior to the initiation of each mercury sample run. This coefficient will be based upon preliminary measurements of gas temperature, flow rate, pressure, and moisture content. Multiplying the K-factor by the measured differential pressure will determine the isokinetic sample rate for each sample point. If a variable changes during a sample run, the coefficient will be adjusted to maintain isokinetic sampling rates. At isokinetic conditions, the velocity of the stack gas entering the nozzle of the extraction system will be equal to the effluent velocity at the sample point.

##### **4.8.1 Sampling by Reference Method 29**

By this method, mercury emissions will be withdrawn isokinetically from the selected sources, collected on a heated filter (maintained at a controlled temperature of  $248 \pm 25^\circ\text{F}$ ), and passed through a series of chilled impingers containing solutions of nitric acid/hydrogen peroxide ( $\text{HNO}_3/\text{H}_2\text{O}_2$ ) and potassium permanganate ( $\text{KMnO}_4$ ) as shown in **Figure 4-2**.

The sample components will be recovered in separate front-half (probe wash and filter) and back-half (impinger solutions) fractions. The front-half and back-half components will be rinsed with 0.1 normal (N) nitric acid ( $\text{HNO}_3$ ) to capture all particulate and collected in their respective containers. The probe wash, digested filter, and aliquots of impinger solutions will be analyzed for mercury by inductively coupled plasma-mass spectroscopy (ICPMS) analysis or cold vapor atomic absorption (CVAA) analysis.



**Figure 4-2 Reference Method 29 Sampling Train**

The condenser assembly will consist of a series of six glass impingers with glass inserts interconnected to each other by glass U tubes, providing a “leak tight” seal with 28/15 ball and socket connections. The first and second impingers will contain  $\text{HNO}_3/\text{H}_2\text{O}_2$ . The third impinger will be left empty. The fourth and fifth impingers will contain  $\text{KMnO}_4$ . The sixth impinger will be filled with a pre weighed amount of silica gel to capture any residual moisture from the sample stream. The impinger train will be set in an ice bath to maintain the extracted gas outlet temperature at or below 70°F. By cooling the sample, all water vapor and gases will be condensed and collected. **Table 4-1** describes the condensate (impinger) train configuration for RM 29 testing including the  $\text{KMnO}_4$  impingers which are exclusive to mercury capture and analysis.

**Table 4-1 Reference Method 29 Condensate (Impinger) Train**

Impinger No.	Contents	Configuration
1	100 ml $\text{HNO}_3/\text{H}_2\text{O}_2$	Straight
2	100 ml $\text{HNO}_3/\text{H}_2\text{O}_2$	Greenburg-Smith
3	Empty	Straight
4	100 ml $\text{KMnO}_4$ (Optional)	Straight
5	100 ml $\text{KMnO}_4$ (Optional)	Straight
6	200 - 300 g Silica Gel	Straight

Prior to sampling, the impingers and their contents will be weighed and the initial weights recorded. Upon completion of sampling, the impingers will be removed from the ice bath and the moisture gain will be determined gravimetrically by subtracting the final weight from the initial weight for each impinger.

Three valid sample runs will be performed for each of the processes being tested. Upon completion of each sample run, the probe will be removed from the exhaust stack and allowed to cool. A leak check of the sampling system will then be performed to verify the integrity of the system. The leak rate must not exceed 0.02 acfm, in order for the test to be considered valid.

Each sample train will be carefully recovered. The filter will be removed from its sample holder with Teflon-coated or non-metallic tweezers and placed in a labeled petri dish. The nozzle, probe, and front-half of the filter holder will be first rinsed with 0.1N HNO<sub>3</sub> to collect any mercury that adhered to the front-half components. The rinse will be quantitatively recovered in a glass sample container. The contents of the first three impingers will be placed in a glass sample jar; the impingers and filter back-half will then be rinsed with 100 ml of 0.1N HNO<sub>3</sub> and added to the same sample jar. The contents of the fourth and fifth impingers will be placed in a glass sample jar; these impingers will then be rinsed with 100 ml of KMnO<sub>4</sub> and added to the same sample jar. The silica gel from the sixth impinger will be weighed to determine moisture gain.

#### 4.8.2 Analyses by Reference Method 29

Each recovered sample will be composed of four fractions: a filter, HNO<sub>3</sub> front-half wash, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> impinger contents with rinse, and KMnO<sub>4</sub> impinger contents and rinse. The filter will be digested and added to the probe wash for mercury analysis. Proportional aliquots of the probe rinse (front-half of the sample train) and samples recovered from impingers 1 through 3 and rinses (back-half of the sample train) will be combined and analyzed for mercury by cold vapor atomic adsorption (CVAA).

#### 4.9 Calculations and Nomenclature

The following section presents the calculations for determining flow rate, molecular weight, and moisture content. In addition, calculations for the determination of particulate concentration and particulate emission rate are provided below. The nomenclature for each calculation also is defined.

##### Calculations

Stack Pressure (in Hg):

$$P_s = P_b + \frac{P_g}{13.6}$$

Volume of Water Collected (scf):

$$V_{wc(std)} = 0.04707 \times MG$$

Gas Meter Volume at Standard Conditions (dscf):

$$V_{m(std)} = V_m \times Y_d \times \left( \frac{T_{std}}{P_{std}} \right) \times \left( \frac{P_b + \frac{\Delta H_{avg}}{13.6}}{T_{m(avg)}} \right)$$

Fractional Moisture Content (dimensionless):

$$B_{ws} = \frac{V_{wc(std)}}{V_{wc(std)} + V_{m(std)}}$$

Moisture Content (%):

$$H_2O \% = B_{ws} \times 100$$

Molecular Weight (dry, lb/lb-mole):

$$M_d = (0.44 \times \% CO_2 + (0.32 \times \% O_2) + (0.28 \times (100 - \% CO_2 - \% O_2)))$$

Molecular Weight (wet, lb/lb-mole):

$$M_s = M_d \times (1 - B_{ws}) + (18 \times B_{ws})$$

Velocity (feet per second):

$$v_s = 85.49 \times C_p \times \sqrt{\Delta p} \times \sqrt{\frac{T_s}{P_s \times M_w}}$$

Flow Rate (actual cubic feet per minute):

$$Q_a = V_s \times A_s \times 60$$

Flow Rate (dry standard cubic feet per minute):

$$Q_s = Q_a \times (1 - B_{ws}) \times 17.64 \times \left( \frac{P_s}{T_s} \right)$$

Percent Isokinetic (%):

$$\% I = \frac{0.09450 \times T_s \times V_{m(std)}}{P_s \times v_s \times A_n \times \Theta \times (1 - B_{ws})}$$

Particulate Concentration (lb/dscf):

$$C_{particulate} = \frac{MG_{particulate}}{453.5924 \times V_{m(std)}}$$

Particulate Emission Rate (lb/hr):

$$E_p = C_{particulate} \times dscfm \times 60$$

Gaseous Pollutant Concentration (dry, ppm):

$$C_{gas} = (C' - C_o) \times \left( \frac{C_{ma}}{C_m - C_o} \right)$$

Gaseous Pollutant Emission Rate (lb/hr):

$$E_{gas} = \frac{C_{gas} \times MW \times Q_s \times 60}{385 \times 1,000,000}$$

Emissions of D/F (ng TEQ/dscm):

$$C_{(D/F)T} = \frac{\sum_{i=1}^n C_{(D/F)i} TEF_i}{V_{m(std)}} \times \frac{ng}{1,000 pg} \times \frac{(20.9 - 7)}{(20.9 - \%O_2)}$$

#### Nomenclature

$A_n$	Cross-Sectional Area of the Nozzle (square feet)
$A_s$	Cross-Sectional Area of the Stack (square feet)
$B_{ws}$	Water Vapor in Gas Stream (proportional by volume)
$C'$	Average Gas Concentration Indicated by Analyzer, dry basis (ppm)
$CC$	Confidence Coefficient (one tailed, 2.5% error)
$C_{gas}$	Corrected Effluent Gas Concentration, dry basis (ppm)
$C_m$	Average of Initial and Final System Calibration Bias Check Responses for the Upscale Calibration Gas (ppm)
$C_{ma}$	Actual Concentration of Upscale Calibration Gas (ppm)
$C_o$	Average of Initial and Final System Calibration Bias Check Responses for the Zero Gas (ppm)
$C_p$	Pitot Tube Coefficient, Dimensionless (0.84 for Type-S)
$C_{particulate}$	Particulate Concentration (lb//dscf)
$C_{(D/F)i}$	Concentration of D/F congener i in sample (pg/liter)
$C_{(D/F)T}$	Total concentration of D/F congeners in sample (ng/liter)
D/F	Stack concentration of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (ng TEQ/dscm)
$\Delta P$	Average Velocity Head of Gas (in WC)
$E_p$	Particulate Emission Rate (lb/hr)
$H_2O\%$	Moisture Content of Gas Stream (%)
$M_d$	Molecular Weight of Stack Gas, dry basis (lb/lb-mole)
$M_s$	Molecular Weight of Stack Gas, wet basis (lb/lb-mole)

MG <sub>particulate</sub>	Particulate mass gain (mg)
MW	Molecular Weight of Pollutant (SO <sub>2</sub> = 64, NO <sub>x</sub> = 46, CO = 28)
ng	nanograms (10 <sup>-9</sup> grams)
pg	picograms (10 <sup>-12</sup> grams)
P <sub>b</sub>	Uncorrected Barometric Pressure (in Hg)
P <sub>g</sub>	Static Pressure of Stack Gas (in WC)
P <sub>s</sub>	Absolute Pressure of Stack Gas (in Hg)
P <sub>std</sub>	Standard Absolute Pressure (29.92 in. Hg)
%CO <sub>2</sub>	Percent Carbon Dioxide, Dry Basis
%O <sub>2</sub>	Percent Oxygen, Dry Basis
%I	Isokinetic sample rate (%)
Q <sub>a</sub>	Actual Flow Rate (acfm)
Q <sub>s</sub>	Dry Standard Flow Rate (dscfm)
RM	Reference Method (RM 6C, RM 7E or RM 10) Data Average (arithmetic mean)
T <sub>m(avg)</sub>	Average DGM Absolute Temperature (°R)
T <sub>s</sub>	Average Stack Gas Temperature (°R)
V <sub>s</sub>	Average Gas Velocity (feet per minute)
T <sub>std</sub>	Standard Absolute Temperature (528 °R)
V <sub>m</sub>	Dry Gas Volume as Measured by the DGM (dcf)
V <sub>m(std)</sub>	Dry Gas Volume Corrected to Standard Conditions (dscf)
V <sub>wc(std)</sub>	Volume of H <sub>2</sub> O Collected in Impingers and Silica Gel Corrected to Standard Conditions (ml)
Y <sub>d</sub>	DGM Calibration Factor
Θ	Sample Time (minutes)

## 5.0 Quality Assurance/Quality Control

### 5.1 Objectives

The objectives of AECOM's QA/QC program are as follows:

- To continually monitor the precision and accuracy of the data being generated for all source emission measurements.
- To implement measures designed to control the precision and accuracy of all data generated for individual sources.
- To maintain permanent records of analytical QC data and equipment calibrations that include traceability and certification.
- To identify, document, and maintain a COC log, which accounts for each method sample collected during each measurement program.

### 5.2 Field Program

All primary, USEPA-approved testing procedures selected for this test program are referenced in the 40 CFR 60, Appendix A. No deviations from these procedures are expected to be necessary. All field personnel responsible for this emission test program will strictly follow the procedures dictated by the applicable test methods.

All field test personnel involved with this test program will be experienced and trained in field sampling methods and procedures. Each field personnel will be assigned key responsibilities in phases of sample collection, sample recovery, COC, and transportation of samples. Basic responsibilities for field personnel include, but are not limited to:

**Record keeping.** Field Personnel will record all pertinent test parameters and relevant observations on the appropriate field data forms.

**Safety requirements.** Field personnel will be familiar with all company safety regulations and will be provided with all the necessary safety equipment.

**Sample handling.** Field personnel will be trained in the proper procedures for handling samples including: use of sample containers, sample preservation, identification, storage of collected samples, and COC.

**Instrumentation.** Specific field personnel will be trained in the proper operation, calibration, trouble shooting, and maintenance of the instrumentation intended for this program. This includes the use of pumps, control console(s), samplers, and instrumentation.

**Quality control (QC).** Field personnel will be trained in all aspects of QC that relate directly to the specific reference method test procedures, sample handling, analyses, and reporting.

Mr. John Rosburg, of AECOM, will be the designated field manager and will be responsible for coordinating testing activities with Pogo and ADEC. He will provide answers to questions concerning test methodology, QC, and all other project aspects. The field manager also will be responsible for delegating work assignments to the members of the test crew, making sure all QA/QC procedures are carried out, and documenting all field activities in a bound log book.

All field instrumentation will be maintained and calibrated according to all applicable USEPA guidelines. Records of instrument maintenance and calibration are kept in historical files and continually updated. Calibrations of all field instrumentation, at a minimum, meet or exceed the mandated procedures stipulated in the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III. All documentation of calibrations is maintained on file at all times. Calibration documentation for the equipment used in this test program will be provided in the Appendices of the test report.

### **5.3 Sample Documentation**

All field data collected for each selected reference method test procedure will be documented on field data forms. Each form, specific to each particular sample run, will include information as to the source tested, date and time of sample collection, analyst(s) performing the test, and all data necessary for test validation. Each field data sheet will be completed by the responsible technician at the time of the test and checked by the Field Manager for accuracy and completeness after each test series. Copies of all raw field data sheets will be included in the appendices of the test report, with the originals maintained in project files at AECOM's Fort Collins office.

Sample containers utilized for the collection and storage of samples will be specific to each test procedure. Filter substrates will be maintained in individually labeled polyethylene Petri dishes sufficient in size to receive the samples unaltered and with the exposed surface protected from sample loss.

Collection of all blanks will be specific to each test performed. The field blanks will be collected at the test location and subjected to the same ambient conditions as the samples. This type of blank will be collected for each reagent used in each test series and analyzed in the same manner as the sample itself.

Each recovered sample will be labeled with standard sample tags and uniquely identified. The tags will provide information regarding the unit tested, sample location, date and time of collection, reagent(s) used, and the test number. The sample container will be sealed, liquid level marked (if applicable), and properly stored until it is transported to the laboratory.

Standard COC forms will be completed before any samples are transported to the laboratory. This procedure is dictated by the USEPA and strictly adhered to by AECOM. Each sample will be tagged with a COC tag, which requires the same information as the field sample label.

### **5.4 Analytical Quality Control**

All analytical procedures used for this program are approved by the USEPA and referenced in 40 CFR 60 (where applicable). All particulate gravimetric analysis will be performed by AECOM at the Fort Collins Air Resources Laboratory. AECOM's QA/QC program meets or exceeds USEPA standards. The D/F XAD-2 resin traps and filters will be prepared by Analytical Perspectives of Wilmington, North Carolina who also will perform the sample analysis. The metals (Cd, Pb, Hg) and HCl analysis will be performed by TestAmerica located in West Sacramento, California.

### **5.5 Data Reduction, Validation, and Reporting**

AECOM has implemented specific measures to ensure that reliable data is generated as a result of the sampling and analytical activities of every field program. The objective of this phase of AECOM's QA/QC program is to follow the proper collection of representative and QA field and analytical data with approved data reduction methods and equations.

All calculations are performed using QA spreadsheets incorporating standard accepted equations, as required by the applicable pollutant specific sampling methodology. Data reduction will be performed by qualified engineers or data analysts familiar with standard engineering practices and approved methods.

Calculation methods and equations, including conversion factors and units, will be defined in this test report to allow the reviewer to easily reproduce the final results from the raw field data and process information provided in the appendices of the report. The final report will include all raw data, QA/QC documentation, and process data collected during the test program. The initial draft of the test report, including both narrative and calculations, will be subjected to review by the project manager and/or Principal-in-Charge, prior to final publication.

# **Appendix A**

## **Field Data Forms**

# RM 1 - Traverse Points For Velocity & Particulate Traverses

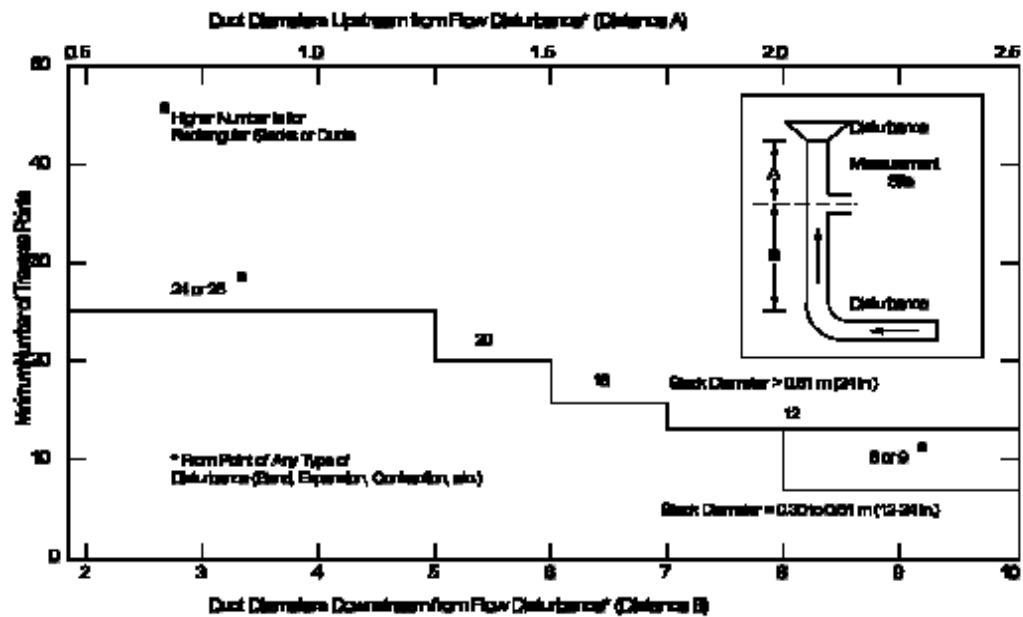


Client \_\_\_\_\_  
Location \_\_\_\_\_  
Source \_\_\_\_\_  
Operator \_\_\_\_\_

Stack Diameter (in) \_\_\_\_\_  
Upstream Distance (in) \_\_\_\_\_ Diameters  
Downstream Distance (in) \_\_\_\_\_ Diameters  
Port Depth (in) \_\_\_\_\_  
Port Diameter (in) \_\_\_\_\_

Location of Traverse Points in Circular Stacks

Traverse Point Number	Number of traverse points (% of stack diameter from inside wall)							Distance (in)	Distance with port (in)
	6	8	10	12	16	20	24		
	1	2	3	4	5	6	7		
1	4.4	3.2	2.6	2.1	1.6	1.3	1.1		
2	14.5	10.5	8.2	6.7	4.9	2.9	3.2		
3	29.6	19.4	14.6	11.8	8.5	6.7	5.5		
4	70.4	32.3	22.6	17.7	12.5	9.7	7.9		
5	85.4	67.7	34.2	25.0	16.9	12.9	10.5		
6	95.6	80.6	66.8	35.6	22.0	16.5	12.2		
7		89.5	77.4	64.4	28.3	20.4	16.1		
8		96.8	85.4	75.0	37.5	25.0	19.4		
9			91.8	82.3	62.5	30.6	23.0		
10			97.4	88.2	71.7	38.8	27.2		
11				93.3	78.0	61.2	32.3		
12				97.9	83.1	69.4	39.8		
13					87.5	75.0	60.2		
14					91.5	79.6	67.7		
15					95.1	83.5	72.8		
16					98.4	87.1	77.0		
17						90.3	80.6		
18						93.3	83.9		
19						96.1	86.8		
20						98.7	88.6		
21							92.1		
22							94.5		
23							96.8		
24							99.9		





Sample Type (circle one):                      Bag                      Integrated                      Continuous                      Other \_\_\_\_\_

Has Orsat or Fyrite unit been successfully leak checked?                      YES/NO

Date	Bag ID/Run Number	% O <sub>2</sub>			% CO <sub>2</sub>		
		Actual Readings		Average	Actual Readings		Average

# ANALYZER CALIBRATION



Client _____	Cylinder #, Supplier, & Conc. _____	Analyzer _____	Model _____
Location _____	_____	Full Scale _____	Serial # _____
Source ID _____	_____	Analyzer _____	Model _____
Operator _____	_____	Full Scale _____	Serial # _____
Date _____	_____	Analyzer _____	Model _____
Initial Cal Time _____	_____	Full Scale _____	Serial # _____
Final Cal Time _____	_____	Analyzer _____	Model _____
	_____	Full Scale _____	Serial # _____
	_____	Analyzer _____	Model _____
	_____	Full Scale _____	Serial # _____

		Cylinder Value (ppm/%)	Analyzer Response (ppm/%)	Absolute Difference (ppm/%)	Percent Difference	
					(% of span)	(Pass/Fail)
Analyzer _____ Initial Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Final Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Analyzer _____ Initial Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Final Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Analyzer _____ Predicted ppm Initial Analyzer Response	Zero					
	Mid-Range					
	Mid-Range					
	High-Range					
Final Analyzer Response Predicted ppm	Zero					
	Mid-Range					
	Mid-Range					
	High-Range					
Analyzer _____ Initial Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Final Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Analyzer _____ Initial Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Final Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Analyzer _____ Initial Analyzer Response	Zero					
	Mid-Range					
	High-Range					
Final Analyzer Response	Zero					
	Mid-Range					
	High-Range					

Cal Error % =abs(CEM-Cylinder)/Span Value X 100  
 Allowable Calibration Error % = 2.0

ANALYZER BIAS



Client: \_\_\_\_\_  
Location: \_\_\_\_\_  
Source ID: \_\_\_\_\_  
Operator: \_\_\_\_\_  
Date: \_\_\_\_\_

Analyzer: \_\_\_\_\_  
Analyzer: \_\_\_\_\_  
Analyzer: \_\_\_\_\_  
Analyzer: \_\_\_\_\_  
Analyzer: \_\_\_\_\_

Span Value: \_\_\_\_\_  
Span Value: \_\_\_\_\_  
Span Value: \_\_\_\_\_  
Span Value: \_\_\_\_\_  
Span Value: \_\_\_\_\_

Run No.	Monitor ID	Analyzer Response (ppm)	Initial Values				Final Values				Calibration Drift	
			Initial Time (military)	System Response (ppm)	Calibration Bias (%)	(Pass/Fail)	Final Time (military)	System Response (ppm)	Calibration Bias (%)	(Pass/Fail)		
Run 1 Zero												
Run 1 Span												
Run 2 Zero												
Run 2 Span												
Run 3 Zero												
Run 3 Span												
Run 1 Zero												
Run 1 Span												
Run 2 Zero												
Run 2 Span												
Run 3 Zero												
Run 3 Span												
Run 1 Zero												
Run 1 Span												
Run 2 Zero												
Run 2 Span												
Run 3 Zero												
Run 3 Span												
Run 1 Zero												
Run 1 Span												
Run 2 Zero												
Run 2 Span												
Run 3 Zero												
Run 3 Span												

System Cal Bias % = (System Cal Response - Analyzer Response) / Span X 100

Calibration Drift = (Final System Response - Initial System Response) / Span X 100

% Allowable = 5.0

% Allowable = 3.0



## ISOKINETIC SAMPLE DATA FORM

Plant:	Filter ID:		
Location:	Ambient Temp. (°F):		
Source I.D.:	Baro. Press. (in. Hg):		
Date:	Static Press. (in H <sub>2</sub> O):		
Flow Traverse Time:	O <sub>2</sub> (%):		
Run No.:	CO <sub>2</sub> (%):		
Operators:	Duct Dia. (in):		
Meter Box I.D.:	B <sub>ws</sub> (assumed):		
Meter Y:	Nozzle Dia. (in):		
Meter Delta H@:	K Factor:		
Probe I.D./ Impinger outlet I.D.:	Leak Check:		
Probe Length/Type:	Pre:	_____	acf _____
Pitot Coeff. (Cp):	Post:	_____	acf _____

Imp.	Moisture	
	Initial	Final
1		
2		
3		
4		
5		
	Net Gain	

[illegible]

### Gravimetric Data Form



Client \_\_\_\_\_

Location \_\_\_\_\_

Probe  
Wash[illegible]

# Particulate Sample Gravimetric Data Form



Client: \_\_\_\_\_  
Location: \_\_\_\_\_  
Sample Location: \_\_\_\_\_  
Run Number: \_\_\_\_\_

Sample Identification-Probe Wash: Yes/No  
Liquid Level Marked - Probe Wash: Yes/No  
Sample Identification-Filter: Yes/No  
Petri Dish Sealed-Filter: Yes/No

## Sample Probe Wash

Beaker I.D.: \_\_\_\_\_  
Density of Rinse (d): \_\_\_\_\_ mg/ml

Blank Mass Concentration (Ca): \_\_\_\_\_ mg/mg  
Sample Volume (Va): \_\_\_\_\_ ml

Date & Time: \_\_\_\_\_  
Date & Time: \_\_\_\_\_

Beaker Final Weight: \_\_\_\_\_ g  
Beaker Final Weight: \_\_\_\_\_ g  
Average Beaker Final Weight: \_\_\_\_\_ g

Date & Time: \_\_\_\_\_  
Date & Time: \_\_\_\_\_

Beaker Tare: \_\_\_\_\_ g  
Beaker Tare: \_\_\_\_\_ g  
Average Beaker Tare: \_\_\_\_\_ g  
Blank Residue Weight (Wa): \_\_\_\_\_ mg  
Mass of Residue (Ma): \_\_\_\_\_ mg

Rinse Mass Gain = \_\_\_\_\_ mg

## Sample Filter

Filter I.D.: \_\_\_\_\_

Date & Time: \_\_\_\_\_  
Date & Time: \_\_\_\_\_

Filter Final Weight: \_\_\_\_\_ g  
Filter Final Weight: \_\_\_\_\_ g  
Average Filter Final Weight: \_\_\_\_\_ g

Date & Time: \_\_\_\_\_  
Date & Time: \_\_\_\_\_

Filter Tare: \_\_\_\_\_ g  
Filter Tare: \_\_\_\_\_ g  
Average Filter Tare: \_\_\_\_\_ g  
Filter Mass Gain: \_\_\_\_\_ mg

Filter Mass Gain = \_\_\_\_\_ mg

Remarks: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Signature of Analyst: \_\_\_\_\_

Signature of Reviewer: \_\_\_\_\_

## **Appendix B**

### **Methodology**

216. In Part 60, Appendix A is amended by revising Methods 1, 1A, 2, 2A, 2B, 2C, 2D, 2E, 3, 3B, 4, 5, 5A, 5B, 5D, 5E, 5F, 5G, 5H, 6, 6A, 6B, 7, 7A, 7B, 7C, 7D, 8, 10A, 10B, 11, 12, 13A, 13B, 14, 15, 15A, 16, 16A, 16B, 17, 18, 19, 21, 22, 24, 24A, 25, 25A, 25B, 25C, 25D, 25E, 26, 26A, 27, 28, 28A, and 29 to read as follows:

**METHOD 1 - SAMPLE AND VELOCITY TRAVERSES  
FOR STATIONARY SOURCES**

**NOTE:** This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test method: Method 2.

*1.0 Scope and Application.*

1.1 Measured Parameters. The purpose of the method is to provide guidance for the selection of sampling ports and traverse points at which sampling for air pollutants will be performed pursuant to regulations set forth in this part. Two procedures are presented: a simplified procedure, and an alternative procedure (see Section 11.5). The magnitude of cyclonic flow of effluent gas in a stack or duct is the only parameter quantitatively measured in the simplified procedure.

1.2 Applicability. This method is applicable to gas streams flowing in ducts, stacks, and flues. This method cannot be used when: (1) the flow is cyclonic or swirling; or (2) a stack is smaller than 0.30 meter (12 in.) in diameter, or  $0.071 \text{ m}^2$  (113 in.<sup>2</sup>) in cross-sectional area. The simplified procedure cannot be used when the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**NOTE:** The requirements of this method must be considered before construction of a new facility from which emissions are to be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases involving variants are subject to approval by the Administrator.

## *2.0 Summary of Method.*

2.1 This method is designed to aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source. A measurement site where the effluent stream is flowing in a known direction is selected, and the cross-section of the

stack is divided into a number of equal areas. Traverse points are then located within each of these equal areas.

*3.0 Definitions.* [Reserved]

*4.0 Interferences.* [Reserved]

*5.0 Safety.*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

*6.0 Equipment and Supplies.*

6.1 Apparatus. The apparatus described below is required only when utilizing the alternative site selection procedure described in Section 11.5 of this method.

6.1.1 Directional Probe. Any directional probe, such as United Sensor Type DA Three-Dimensional Directional Probe, capable of measuring both the pitch and yaw angles of gas flows is acceptable. Before using the probe, assign an identification number to the directional probe, and permanently mark or engrave the number on the body of the probe. The pressure holes of directional probes are susceptible to plugging when used in particulate-laden gas

streams. Therefore, a procedure for cleaning the pressure holes by "back-purging" with pressurized air is required.

6.1.1.2 Differential Pressure Gauges. Inclined manometers, U-tube manometers, or other differential pressure gauges (e.g., magnehelic gauges) that meet the specifications described in Method 2, Section 6.2.

**NOTE:** If the differential pressure gauge produces both negative and positive readings, then both negative and positive pressure readings shall be calibrated at a minimum of three points as specified in Method 2, Section 6.2.

7.0 *Reagents and Standards.* [Reserved]

8.0 *Sample Collection, Preservation, Storage, and Transport.* [Reserved]

9.0 *Quality Control.* [Reserved]

10.0 *Calibration and Standardization.* [Reserved]

11.0 *Procedure.*

11.1 Selection of Measurement Site.

11.1.1 Sampling and/or velocity measurements are performed at a site located at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack, or from a visible flame. If necessary, an alternative location may be selected, at a position at least

two stack or duct diameters downstream and a half diameter upstream from any flow disturbance.

11.1.2 An alternative procedure is available for determining the acceptability of a measurement location not meeting the criteria above. This procedure described in Section 11.5 allows for the determination of gas flow angles at the sampling points and comparison of the measured results with acceptability criteria.

#### 11.2 Determining the Number of Traverse Points.

##### 11.2.1 Particulate Traverses.

11.2.1.1 When the eight- and two-diameter criterion can be met, the minimum number of traverse points shall be: (1) twelve, for circular or rectangular stacks with diameters (or equivalent diameters) greater than 0.61 meter (24 in.); (2) eight, for circular stacks with diameters between 0.30 and 0.61 meter (12 and 24 in.); and (3) nine, for rectangular stacks with equivalent diameters between 0.30 and 0.61 meter (12 and 24 in.).

11.2.1.2 When the eight- and two-diameter criterion cannot be met, the minimum number of traverse points is determined from Figure 1-1. Before referring to the figure, however, determine the distances from the measurement site to the nearest upstream and downstream disturbances, and divide each distance by the stack diameter or equivalent

diameter, to determine the distance in terms of the number of duct diameters. Then, determine from Figure 1-1 the minimum number of traverse points that corresponds: (1) to the number of duct diameters upstream; and (2) to the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, so that for circular stacks the number is a multiple of 4, and for rectangular stacks, the number is one of those shown in Table 1-1.

11.2.2 Velocity (Non-Particulate) Traverses. When velocity or volumetric flow rate is to be determined (but not particulate matter), the same procedure as that used for particulate traverses (Section 11.2.1) is followed, except that Figure 1-2 may be used instead of Figure 1-1.

11.3 Cross-Sectional Layout and Location of Traverse Points.

11.3.1 Circular Stacks.

11.3.1.1 Locate the traverse points on two perpendicular diameters according to Table 1-2 and the example shown in Figure 1-3. Any equation (see examples in References 2 and 3 in Section 16.0) that gives the same values as those in Table 1-2 may be used in lieu of Table 1-2.

11.3.1.2 For particulate traverses, one of the diameters must coincide with the plane containing the greatest expected concentration variation (e.g., after bends); one diameter shall be congruent to the direction of the bend. This requirement becomes less critical as the distance from the disturbance increases; therefore, other diameter locations may be used, subject to the approval of the Administrator.

11.3.1.3 In addition, for elliptical stacks having unequal perpendicular diameters, separate traverse points shall be calculated and located along each diameter. To determine the cross-sectional area of the elliptical stack, use the following equation:

$$\text{Square Area} = D_1 \times D_2 \times 0.7854$$

Where:  $D_1$  = Stack diameter 1

$D_2$  = Stack diameter 2

11.3.1.4 In addition, for stacks having diameters greater than 0.61 m (24 in.), no traverse points shall be within 2.5 centimeters (1.00 in.) of the stack walls; and for stack diameters equal to or less than 0.61 m (24 in.), no traverse points shall be located within 1.3 cm (0.50 in.) of the stack walls. To meet these criteria, observe the procedures given below.

11.3.2 Stacks With Diameters Greater Than 0.61 m

(24 in.).

11.3.2.1 When any of the traverse points as located in Section 11.3.1 fall within 2.5 cm (1.0 in.) of the stack walls, relocate them away from the stack walls to: (1) a distance of 2.5 cm (1.0 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the "adjusted" traverse points.

11.3.2.2 Whenever two successive traverse points are combined to form a single adjusted traverse point, treat the adjusted point as two separate traverse points, both in the sampling and/or velocity measurement procedure, and in recording of the data.

11.3.3 Stacks With Diameters Equal To or Less Than 0.61 m (24 in.). Follow the procedure in Section 11.3.1.1, noting only that any "adjusted" points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

11.3.4 Rectangular Stacks.

11.3.4.1 Determine the number of traverse points as explained in Sections 11.1 and 11.2 of this method. From Table 1-1, determine the grid configuration. Divide the stack cross-section into as many equal rectangular elemental

areas as traverse points, and then locate a traverse point at the centroid of each equal area according to the example in Figure 1-4.

11.3.4.2 To use more than the minimum number of traverse points, expand the "minimum number of traverse points" matrix (see Table 1-1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4 x 3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9 x 4 or 12 x 3, and would not necessarily have to be 6 x 6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

11.3.4.3 The situation of traverse points being too close to the stack walls is not expected to arise with rectangular stacks. If this problem should ever arise, the Administrator must be contacted for resolution of the matter.

#### 11.4 Verification of Absence of Cyclonic Flow.

11.4.1 In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers,

or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

11.4.2 Level and zero the manometer. Connect a Type S pitot tube to the manometer and leak-check system. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane; when the Type S pitot tube is in this position, it is at "0° reference." Note the differential pressure ( $\Delta p$ ) reading at each traverse point. If a null (zero) pitot reading is obtained at 0° reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0° reference, rotate the pitot tube (up to  $\pm 90^\circ$  yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle ( $\theta$ ) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of  $\theta$ ; assign  $\theta$  values of 0° to those points for which no rotation was required, and include these in the overall average. If the average value of  $\theta$  is greater than 20°, the overall flow condition in the

stack is unacceptable, and alternative methodology, subject to the approval of the Administrator, must be used to perform accurate sample and velocity traverses.

11.5 The alternative site selection procedure may be used to determine the rotation angles in lieu of the procedure outlined in Section 11.4.

11.5.1 Alternative Measurement Site Selection Procedure. This alternative applies to sources where measurement locations are less than 2 equivalent or duct diameters downstream or less than one-half duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 in. in diameter where blockage and wall effects are minimal. A directional flow-sensing probe is used to measure pitch and yaw angles of the gas flow at 40 or more traverse points; the resultant angle is calculated and compared with acceptable criteria for mean and standard deviation.

**NOTE:** Both the pitch and yaw angles are measured from a line passing through the traverse point and parallel to the stack axis. The pitch angle is the angle of the gas flow component in the plane that INCLUDES the traverse line and is parallel to the stack axis. The yaw angle is the angle of the gas flow component in the plane PERPENDICULAR to the traverse line at the traverse point and is measured

from the line passing through the traverse point and parallel to the stack axis.

11.5.2 Traverse Points. Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations. Follow the procedure outlined in Section 11.3 and Table 1-1 or 1-2 for the location and layout of the traverse points. If the measurement location is determined to be acceptable according to the criteria in this alternative procedure, use the same traverse point number and locations for sampling and velocity measurements.

#### 11.5.3 Measurement Procedure.

11.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer. Capillary tubing or surge tanks may be used to dampen pressure fluctuations. It is recommended, but not required, that a pretest leak check be conducted. To perform a leak check, pressurize or use suction on the impact opening until a reading of at least 7.6 cm (3 in.) H<sub>2</sub>O registers on the differential pressure gauge, then plug the impact opening. The pressure of a leak-free system will remain stable for at least 15 seconds.

11.5.3.2 Level and zero the manometers. Since the manometer level and zero may drift because of vibrations and

temperature changes, periodically check the level and zero during the traverse.

11.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point. Complete a "back-purge" of the pressure lines and the impact openings prior to measurements of each traverse point.

11.5.3.4 A post-test check as described in Section 11.5.3.1 is required. If the criteria for a leak-free system are not met, repair the equipment, and repeat the flow angle measurements.

11.5.4 Calibration. Use a flow system as described in Sections 10.1.2.1 and 10.1.2.2 of Method 2. In addition, the flow system shall have the capacity to generate two test-section velocities: one between 365 and 730 m/min (1,200 and 2,400 ft/min) and one between 730 and 1,100 m/min (2,400 and 3,600 ft/min).

11.5.4.1 Cut two entry ports in the test section. The axes through the entry ports shall be perpendicular to each other and intersect in the centroid of the test

section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should be constructed of plexiglass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test section.

11.5.4.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure outlined in Section 11.4 for cyclonic flow determination to measure the gas flow angles at the centroid of the test section from two test ports located  $90^\circ$  apart. The gas flow angle measured in each port must be  $\pm 2^\circ$  of  $0^\circ$ . Straightening vanes should be installed, if necessary, to meet this criterion.

11.5.4.3 Pitch Angle Calibration. Perform a calibration traverse according to the manufacturer's recommended protocol in  $5^\circ$  increments for angles from  $-60^\circ$  to  $+60^\circ$  at one velocity in each of the two ranges specified above. Average the pressure ratio values obtained for each angle in the two flow ranges, and plot a calibration curve

with the average values of the pressure ratio (or other suitable measurement factor as recommended by the manufacturer) versus the pitch angle. Draw a smooth line through the data points. Plot also the data values for each traverse point. Determine the differences between the measured data values and the angle from the calibration curve at the same pressure ratio. The difference at each comparison must be within  $2^\circ$  for angles between  $0^\circ$  and  $40^\circ$  and within  $3^\circ$  for angles between  $40^\circ$  and  $60^\circ$ .

11.5.4.4 Yaw Angle Calibration. Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening. To determine the accuracy of measurements of the yaw angle, only the zero or null position need be calibrated as follows: Place the directional probe in the test section, and rotate the probe until the zero position is found. With a protractor or other angle measuring device, measure the angle indicated by the yaw angle indicator on the three-dimensional probe. This should be within  $2^\circ$  of  $0^\circ$ . Repeat this measurement for any other points along the length of the pitot where yaw angle measurements could be read in order to account for variations in the pitot markings used to indicate pitot head positions.

## 12.0 Data Analysis and Calculations.

### 12.1 Nomenclature.

L = length

n = total number of traverse points.

P<sub>i</sub> = pitch angle at traverse point i, degree.

R<sub>avg</sub> = average resultant angle, degree.

R<sub>i</sub> = resultant angle at traverse point i, degree.

S<sub>d</sub> = standard deviation, degree.

W = width.

Y<sub>i</sub> = yaw angle at traverse point i, degree.

12.2 For a rectangular cross section, an equivalent diameter (D<sub>e</sub>) shall be calculated using the following equation, to determine the upstream and downstream distances:

$$D_e = \frac{2 (L) (W)}{L + W} \quad \text{Eq. 1-1}$$

12.3 If use of the alternative site selection procedure (Section 11.5 of this method) is required, perform the following calculations using the equations below: the resultant angle at each traverse point, the average resultant angle, and the standard deviation. Complete the calculations retaining at least one extra significant figure beyond that of the acquired data. Round the values after the final calculations.

12.3.1 Calculate the resultant angle at each traverse point:

$$R_i = \arccos [(\cos Y_i)(\cos P_i)] \quad \text{Eq. 1-2}$$

12.3.2 Calculate the average resultant for the measurements:

$$R_{\text{avg}} = \sum R_i / n \quad \text{Eq. 1-3}$$

12.3.3 Calculate the standard deviations:

$$S_d = \sqrt{\frac{\sum_{i=1}^n (R_i - R_{\text{avg}})^2}{(n-1)}} \quad \text{Eq. 1-4}$$

12.3.4 Acceptability Criteria. The measurement location is acceptable if  $R_{\text{avg}} \leq 20^\circ$  and  $S_d \leq 10^\circ$ .

13.0 *Method Performance.* [Reserved]

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References.*

1. Determining Dust Concentration in a Gas Stream, ASME Performance Test Code No. 27. New York. 1957.

2. DeVorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District. Los Angeles, CA. November 1963.

3. Methods for Determining of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division

of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP-50. 1968.

4. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Book of ASTM Standards, Part 23. ASTM Designation D 2928-71. Philadelphia, PA. 1971.

5. Hanson, H.A., et al. Particulate Sampling Strategies for Large Power Plants Including Nonuniform Flow. USEPA, ORD, ESRL, Research Triangle Park, NC. EPA-600/2-76-170. June 1976.

6. Entropy Environmentalists, Inc. Determination of the Optimum Number of Sampling Points: An Analysis of Method 1 Criteria. Environmental Protection Agency. Research Triangle Park, NC. EPA Contract No. 68-01-3172, Task 7.

7. Hanson, H.A., R.J. Davini, J.K. Morgan, and A.A. Iversen. Particulate Sampling Strategies for Large Power Plants Including Nonuniform Flow. USEPA, Research Triangle Park, NC. Publication No. EPA-600/2-76-170. June 1976. 350 pp.

8. Brooks, E.F., and R.L. Williams. Flow and Gas Sampling Manual. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/2-76-203. July 1976. 93 pp.

9. Entropy Environmentalists, Inc. Traverse Point Study. EPA Contract No. 68-02-3172. June 1977. 19 pp.

10. Brown, J. and K. Yu. Test Report: Particulate Sampling Strategy in Circular Ducts. Emission Measurement Branch. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. July 31, 1980. 12 pp.

11. Hawksley, P.G.W., S. Badzioch, and J.H. Blackett. Measurement of Solids in Flue Gases. Leatherhead, England, The British Coal Utilisation Research Association. 1961. pp. 129-133.

12. Knapp, K.T. The Number of Sampling Points Needed for Representative Source Sampling. In: Proceedings of the Fourth National Conference on Energy and Environment. Theodore, L. et al. (ed). Dayton, Dayton Section of the American Institute of Chemical Engineers. October 3-7, 1976. pp. 563-568.

13. Smith, W.S. and D.J. Grove. A Proposed Extension of EPA Method 1 Criteria. Pollution Engineering. XV (8):36-37. August 1983.

14. Gerhart, P.M. and M.J. Dorsey. Investigation of Field Test Procedures for Large Fans. University of Akron. Akron, OH. (EPRI Contract CS-1651). Final Report (RP-1649-5). December 1980.

15. Smith, W.S. and D.J. Grove. A New Look at Isokinetic Sampling - Theory and Applications. Source Evaluation Society Newsletter. VIII(3):19-24. August 1983.

*17.0 Tables, Diagrams, Flowcharts, and Validation Data.*

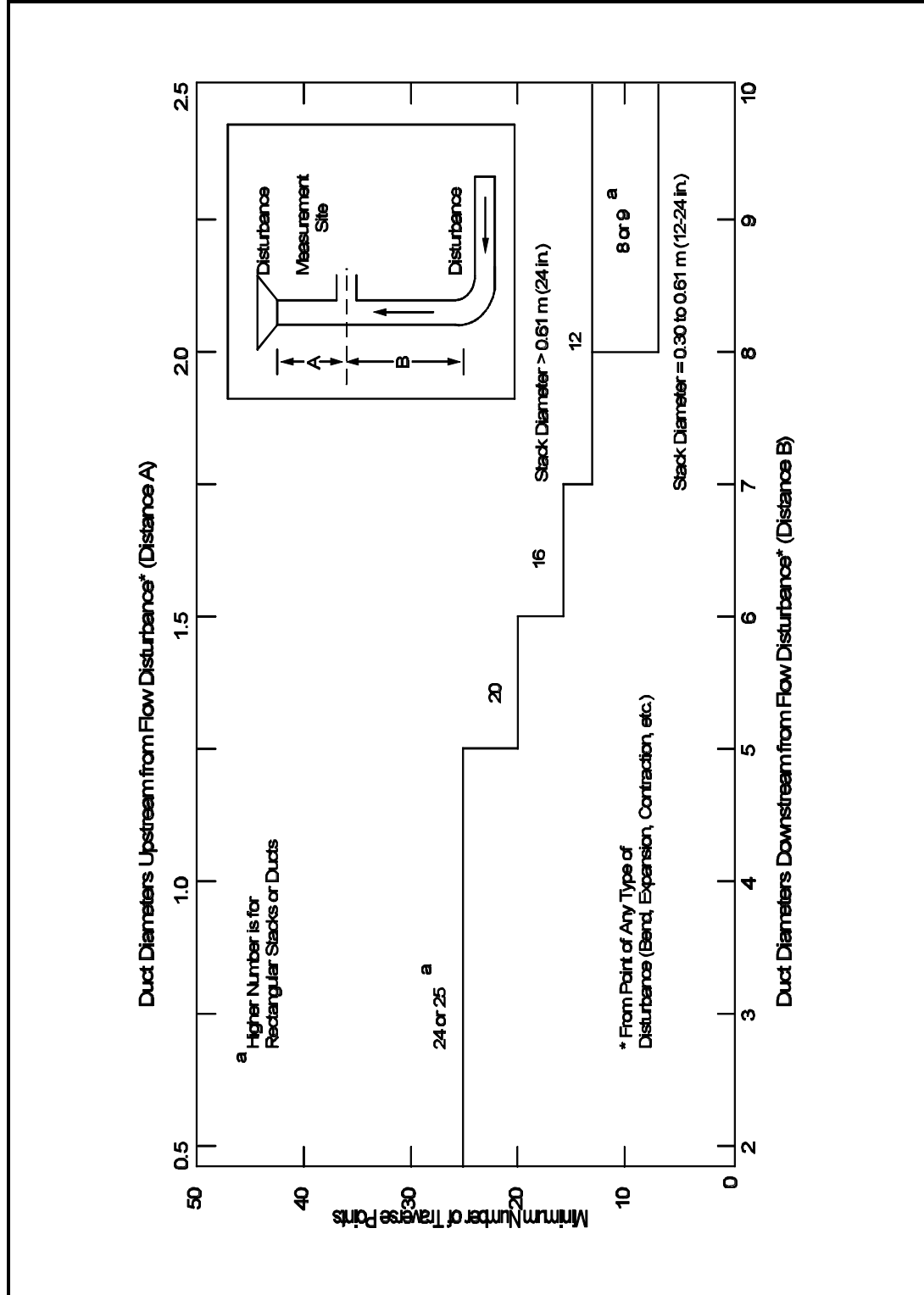


Figure 1-1. Minimum number of traverse points for particulate traverses.

TABLE 1-1. CROSS-SECTION LAYOUT FOR  
RECTANGULAR STACKS

Number of tranverse points layout	Matrix
9 . . . . . 3 x 3	
12 . . . . . 4 x 3	
16 . . . . . 4 x 4	
20 . . . . . 5 x 4	
25 . . . . . 5 x 5	
30 . . . . . 6 x 5	
36 . . . . . 6 x 6	
42 . . . . . 7 x 6	
49 . . . . . 7 x 7	

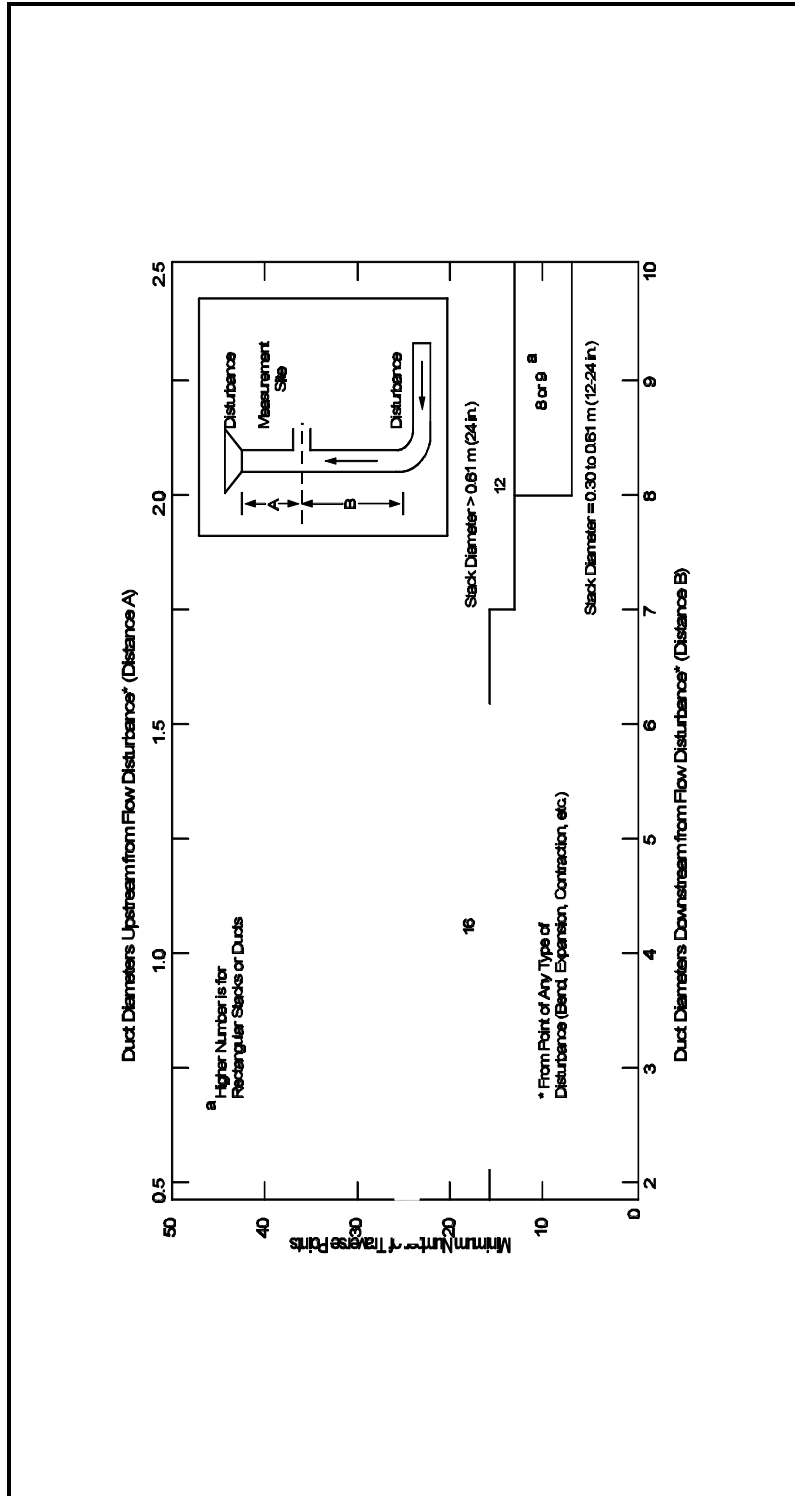
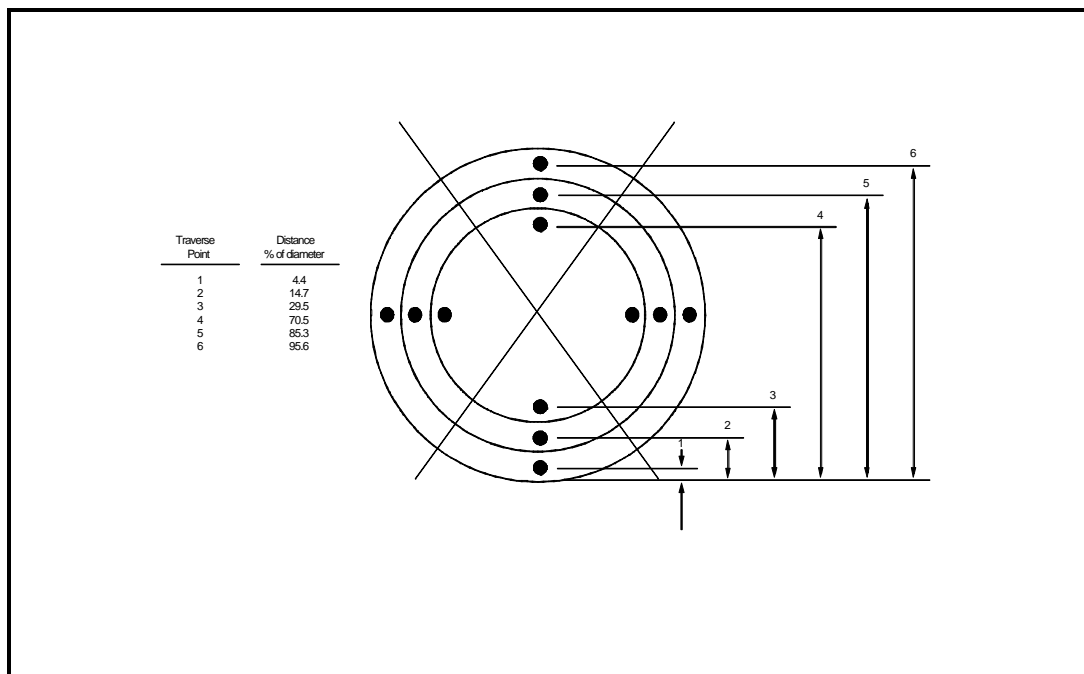
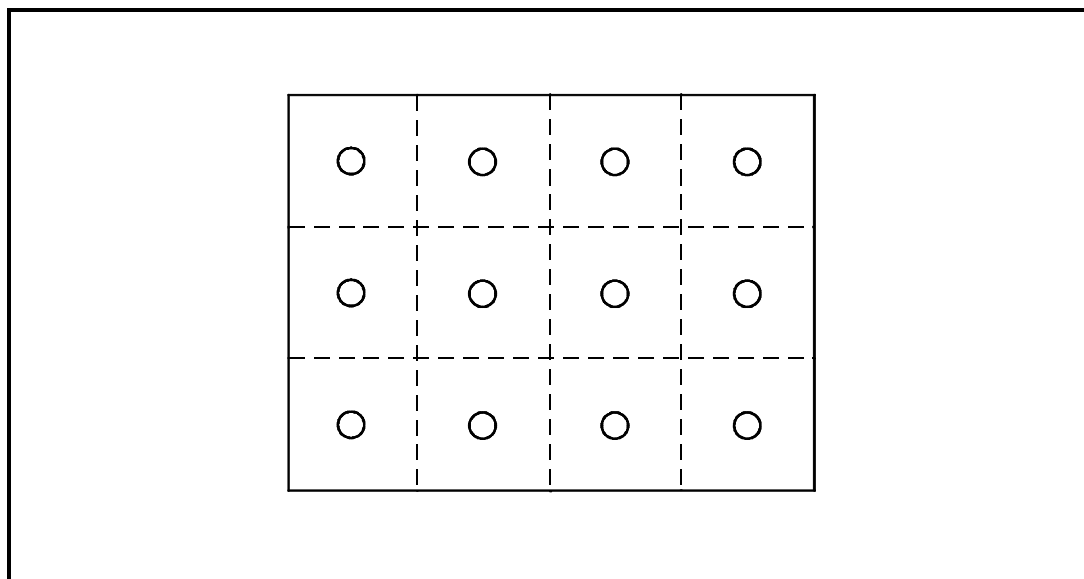


Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

[illegible]



**Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points.**



**Figure 1-4. Example showing rectangular stack cross section divided into 12 equal areas, with traverse points at centroid of each area.**

**METHOD 2 - DETERMINATION OF STACK GAS VELOCITY AND  
VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)**

**NOTE:** This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test method: Method 1.

*1.0 Scope and Application.*

1.1 This method is applicable for the determination of the average velocity and the volumetric flow rate of a gas stream.

1.2 This method is not applicable at measurement sites that fail to meet the criteria of Method 1, Section 11.1. Also, the method cannot be used for direct measurement in cyclonic or swirling gas streams; Section 11.4 of Method 1 shows how to determine cyclonic or swirling flow conditions. When unacceptable conditions exist, alternative procedures, subject to the approval of the Administrator, must be employed to produce accurate flow rate determinations. Examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically,

or (3) to move to another measurement site at which the flow is acceptable.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## *2.0 Summary of Method.*

2.1 The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube.

3.0 *Definitions.* [Reserved]

4.0 *Interferences.* [Reserved]

## *5.0 Safety.*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

## *6.0 Equipment and Supplies.*

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to

approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

#### 6.1 Type S Pitot Tube.

6.1.1 Pitot tube made of metal tubing (e.g., stainless steel) as shown in Figure 2-1. It is recommended that the external tubing diameter (dimension  $D_t$ , Figure 2-2b) be between 0.48 and 0.95 cm (3/16 and 3/8 inch). There shall be an equal distance from the base of each leg of the pitot tube to its face-opening plane (dimensions  $P_A$  and  $P_B$ , Figure 2-2b); it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned as shown in Figure 2-2; however, slight misalignments of the openings are permissible (see Figure 2-3).

6.1.2 The Type S pitot tube shall have a known coefficient, determined as outlined in Section 10.0. An identification number shall be assigned to the pitot tube; this number shall be permanently marked or engraved on the body of the tube. A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of Sections 6.7 and 10.2. Note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams.

Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period. This can be accomplished by comparing the velocity head ( $\rho$ ) measurement recorded at a selected traverse point (readable  $\rho$  value) with a second  $\rho$  measurement recorded after "back purging" with pressurized air to clean the impact and static holes of the standard pitot tube. If the before and after  $\rho$  measurements are within 5 percent, then the traverse data are acceptable. Otherwise, the data should be rejected and the traverse measurements redone. Note that the selected traverse point should be one that demonstrates a readable  $\rho$  value. If "back purging" at regular intervals is part of a routine procedure, then comparative  $\rho$  measurements shall be conducted as above for the last two traverse points that exhibit suitable  $\rho$  measurements.

6.2 Differential Pressure Gauge. An inclined manometer or equivalent device. Most sampling trains are equipped with a 10 in. (water column) inclined-vertical manometer, having 0.01 in.  $H_2O$  divisions on the 0 to 1 in. inclined scale, and 0.1 in.  $H_2O$  divisions on the 1 to 10 in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of  $\rho$  values as low as 1.27 mm (0.05 in.)  $H_2O$ . However, a

differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all  $\Delta p$  readings at the traverse points in the stack is less than 1.27 mm (0.05 in.)  $H_2O$ ; (2) for traverses of 12 or more points, more than 10 percent of the individual  $\Delta p$  readings are below 1.27 mm (0.05 in.)  $H_2O$ ; or (3) for traverses of fewer than 12 points, more than one  $\Delta p$  reading is below 1.27 mm (0.05 in.)  $H_2O$ . Reference 18 (see Section 17.0) describes commercially available instrumentation for the measurement of low-range gas velocities.

6.2.1 As an alternative to criteria (1) through (3) above, Equation 2-1 (Section 12.2) may be used to determine the necessity of using a more sensitive differential pressure gauge. If  $T$  is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

**NOTE:** If differential pressure gauges other than inclined manometers are used (e.g., magnehelic gauges), their calibration must be checked after each test series. To check the calibration of a differential pressure gauge, compare  $\Delta p$  readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of  $\Delta p$  values in the stack. If, at

each point, the values of  $p$  as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured  $p$  values and final results shall be used, subject to the approval of the Administrator.

6.3 Temperature Sensor. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge capable of measuring temperatures to within 1.5 percent of the minimum absolute stack temperature. The temperature sensor shall be attached to the pitot tube such that the sensor tip does not touch any metal; the gauge shall be in an interference-free arrangement with respect to the pitot tube face openings (see Figure 2-1 and Figure 2-4). Alternative positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of Section 10.0. Provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the temperature gauge need not be attached to the pitot tube. This alternative is subject to the approval of the Administrator.

6.4 Pressure Probe and Gauge. A piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg. The

static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may also be used as the pressure probe.

6.5 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.54 mm (0.1 in.) Hg.

**NOTE:** The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm (0.1 in.) Hg per 30 m (100 ft) elevation increase or plus 2.5 mm (0.1 in.) Hg per 30 m (100 ft.) for elevation decrease.

6.6 Gas Density Determination Equipment. Method 3 equipment, if needed (see Section 8.6), to determine the stack gas dry molecular weight, and Method 4 (reference method) or Method 5 equipment for moisture content determination. Other methods may be used subject to approval of the Administrator.

6.7 Calibration Pitot Tube. When calibration of the Type S pitot tube is necessary (see Section 10.1), a standard pitot tube shall be used for a reference. The

standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Institute of Standards and Technology (NIST), Gaithersburg MD 20899, (301) 975-2002, or (2) by calibration against another standard pitot tube with an NIST-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in Sections 6.7.1 through 6.7.5 below and illustrated in Figure 2-5 (see also References 7, 8, and 17 in Section 17.0) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of  $0.99 \pm 0.01$ .

#### 6.7.1 Standard Pitot Design.

6.7.1.1 Hemispherical (shown in Figure 2-5), ellipsoidal, or conical tip.

6.7.1.2 A minimum of six diameters straight run (based upon D, the external diameter of the tube) between the tip and the static pressure holes.

6.7.1.3 A minimum of eight diameters straight run between the static pressure holes and the centerline of the external tube, following the 90° bend.

6.7.1.4 Static pressure holes of equal size (approximately 0.1 D), equally spaced in a piezometer ring configuration.

6.7.1.5 90° bend, with curved or mitered junction.

6.8 Differential Pressure Gauge for Type S Pitot Tube Calibration. An inclined manometer or equivalent. If the single-velocity calibration technique is employed (see Section 10.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.127 mm (0.005 in.)  $H_2O$ . For multivelocity calibrations, the gauge shall be readable to the nearest 0.127 mm (0.005 in.)  $H_2O$  for  $p$  values between 1.27 and 25.4 mm (0.05 and 1.00 in.)  $H_2O$ , and to the nearest 1.27 mm (0.05 in.)  $H_2O$  for  $p$  values above 25.4 mm (1.00 in.)  $H_2O$ . A special, more sensitive gauge will be required to read  $p$  values below 1.27 mm (0.05 in.)  $H_2O$  (see Reference 18 in Section 16.0).

7.0 *Reagents and Standards.* [Reserved]

8.0 *Sample Collection and Analysis.*

8.1 Set up the apparatus as shown in Figure 2-1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen  $p$  fluctuations. It is recommended, but not required, that a pretest leak-check be conducted as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3.0 in.)  $H_2O$  velocity head registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the

minimum of 7.6 cm (3.0 in.) H<sub>2</sub>O. Other leak-check procedures, subject to the approval of the Administrator, may be used.

8.2 Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse (at least once per hour). Record all necessary data on a form similar to that shown in Figure 2-6.

8.3 Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of  $\Delta p$  values encountered (see Section 6.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the  $\Delta p$  and temperature readings at each traverse point. Conduct a post-test leak-check (mandatory), as described in Section 8.1 above, to validate the traverse run.

8.4 Measure the static pressure in the stack. One reading is usually adequate.

8.5 Determine the atmospheric pressure.

8.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO<sub>2</sub>, O<sub>2</sub>, CO, and N<sub>2</sub>, use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other

methods, subject to the approval of the Administrator, must be used.

8.7 Obtain the moisture content from Method 4 (reference method, or equivalent) or from Method 5.

8.8 Determine the cross-sectional area of the stack or duct at the sampling location. Whenever possible, physically measure the stack dimensions rather than using blueprints. Do not assume that stack diameters are equal. Measure each diameter distance to verify its dimensions.

#### *9.0 Quality Control.*

Section	Quality Control Measure	Effect
10.1-10.4	Sampling equipment calibration	Ensure accurate measurement of stack gas flow rate, sample volume

#### *10.0 Calibration and Standardization.*

10.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figures 2-2 and 2-3. The pitot tube shall not be used if it fails to meet these alignment specifications. After verifying the face opening alignment, measure and record the following dimensions of the pitot tube: (a) the external tubing diameter (dimension  $D_t$ , Figure 2-2b); and (b) the base-to-opening plane distances (dimensions  $P_A$  and  $P_B$ , Figure 2-2b).

If  $D_t$  is between 0.48 and 0.95 cm (3/16 and 3/8 in.), and if  $P_A$  and  $P_B$  are equal and between 1.05 and 1.50  $D_t$ , there are two possible options: (1) the pitot tube may be calibrated according to the procedure outlined in Sections 10.1.2 through 10.1.5, or (2) a baseline (isolated tube) coefficient value of 0.84 may be assigned to the pitot tube. Note, however, that if the pitot tube is part of an assembly, calibration may still be required, despite knowledge of the baseline coefficient value (see Section 10.1.1). If  $D_t$ ,  $P_A$ , and  $P_B$  are outside the specified limits, the pitot tube must be calibrated as outlined in Sections 10.1.2 through 10.1.5.

10.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (e.g., thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Reference 9 in Section 17.0); therefore, an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such

that aerodynamic interference effects are eliminated. Figures 2-4, 2-7, and 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-4, 2-7, and 2-8 shall be calibrated according to the procedure outlined in Sections 10.1.2 through 10.1.5, and prior to calibration, the values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

**NOTE:** Do not use a Type S pitot tube assembly that is constructed such that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle (see Figure 2-6B).

10.1.2 Calibration Setup. If the Type S pitot tube is to be calibrated, one leg of the tube shall be permanently marked A, and the other, B. Calibration shall be performed in a flow system having the following essential design features:

10.1.2.1 The flowing gas stream must be confined to a duct of definite cross-sectional area, either circular or rectangular. For circular cross sections, the minimum duct diameter shall be 30.48 cm (12 in.); for rectangular cross

sections, the width (shorter side) shall be at least 25.4 cm (10 in.).

10.1.2.2 The cross-sectional area of the calibration duct must be constant over a distance of 10 or more duct diameters. For a rectangular cross section, use an equivalent diameter, calculated according to Equation 2-2 (see Section 12.3), to determine the number of duct diameters. To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least eight diameters downstream and two diameters upstream from the nearest disturbances.

**NOTE:** The eight- and two-diameter criteria are not absolute; other test section locations may be used (subject to approval of the Administrator), provided that the flow at the test site has been demonstrated to be or found stable and parallel to the duct axis.

10.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 910 m/min (3,000 ft/min). This velocity must be constant with time to guarantee steady flow during calibration. Note that Type S pitot tube coefficients obtained by single-velocity calibration at 910 m/min (3,000 ft/min) will generally be valid to  $\pm 3$  percent for the measurement of velocities above

300 m/min (1,000 ft/min) and to  $\pm 6$  percent for the measurement of velocities between 180 and 300 m/min (600 and 1,000 ft/min). If a more precise correlation between the pitot tube coefficient,  $(C_p)$ , and velocity is desired, the flow system should have the capacity to generate at least four distinct, time-invariant test-section velocities covering the velocity range from 180 to 1,500 m/min (600 to 5,000 ft/min), and calibration data shall be taken at regular velocity intervals over this range (see References 9 and 14 in Section 17.0 for details).

10.1.2.4 Two entry ports, one for each of the standard and Type S pitot tubes, shall be cut in the test section. The standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of Plexiglas™ or some other transparent material.

10.1.3 Calibration Procedure. Note that this procedure is a general one and must not be used without first referring to the special considerations presented in Section 10.1.5. Note also that this procedure applies only to single-velocity calibration. To obtain calibration data

for the A and B sides of the Type S pitot tube, proceed as follows:

10.1.3.1 Make sure that the manometer is properly filled and that the oil is free from contamination and is of the proper density. Inspect and leak-check all pitot lines; repair or replace if necessary.

10.1.3.2 Level and zero the manometer. Switch on the fan, and allow the flow to stabilize. Seal the Type S pitot tube entry port.

10.1.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in Section 10.1.5.1), and align the tube so that its tip is pointed directly into the flow. Particular care should be taken in aligning the tube to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

10.1.3.4 Read  $p_{std}$ , and record its value in a data table similar to the one shown in Figure 2-9. Remove the standard pitot tube from the duct, and disconnect it from the manometer. Seal the standard entry port.

10.1.3.5 Connect the Type S pitot tube to the manometer and leak-check. Open the Type S tube entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its A side impact opening is at the same point as was the standard pitot tube and is pointed

directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

10.1.3.6 Read  $p_s$ , and enter its value in the data table. Remove the Type S pitot tube from the duct, and disconnect it from the manometer.

10.1.3.7 Repeat Steps 10.1.3.3 through 10.1.3.6 until three pairs of  $p$  readings have been obtained for the A side of the Type S pitot tube.

10.1.3.8 Repeat Steps 10.1.3.3 through 10.1.3.7 for the B side of the Type S pitot tube.

10.1.3.9 Perform calculations as described in Section 12.4. Use the Type S pitot tube only if the values of  $F_A$  and  $F_B$  are less than or equal to 0.01 and if the absolute value of the difference between  $C_{p(A)}$  and  $C_{p(B)}$  is 0.01 or less.

10.1.4 Special Considerations.

10.1.4.1 Selection of Calibration Point.

10.1.4.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Section 10.1.3. The Type S pitot coefficients measured or calculated, [i.e.  $C_{p(A)}$  and  $C_{p(B)}$ ] will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free

from aerodynamic interference effects (see Figures 2-4, 2-7, and 2-8).

10.1.4.1.2 For Type S pitot tube-thermocouple combinations (without probe assembly), select a calibration point at or near the center of the duct, and follow the procedures outlined in Section 10.1.3. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination is used by itself or with other components in an interference-free arrangement (Figures 2-4, 2-7, and 2-8).

10.1.4.1.3 For Type S pitot tube combinations with complete probe assemblies, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area interference and blockage and yield incorrect coefficient values (Reference 9 in Section 17.0). Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary. The actual blockage effect will be negligible when the theoretical blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and 3 percent or less for assemblies with external sheaths (Figure 2-10b).

10.1.4.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (*i.e.*, those in which the pitot-nozzle separation distance fails to meet the specifications illustrated in Figure 2-7A), the value of  $C_{p(s)}$  depends upon the amount of free space between the tube and nozzle and, therefore, is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes ( $>0.635$  cm or  $1/4$  in.) are not ordinarily used for isokinetic sampling at velocities around 910 m/min (3,000 ft/min), which is the calibration velocity. Note also that it is not necessary to draw an isokinetic sample during calibration (see Reference 19 in Section 17.0).

10.1.4.3 For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side which will face the flow). The pitot tube must still meet the alignment specifications of Figure 2-2 or 2-3, however, and must have an average deviation (**F**) value of 0.01 or less (see Section 10.1.4.4).

10.1.5 Field Use and Recalibration.

10.1.5.1 Field Use.

10.1.5.1.1 When a Type S pitot tube (isolated or in an assembly) is used in the field, the appropriate coefficient value (whether assigned or obtained by calibration) shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A side coefficient shall be used when the A side of the tube faces the flow, and the B side coefficient shall be used when the B side faces the flow. Alternatively, the arithmetic average of the A and B side coefficient values may be used, irrespective of which side faces the flow.

10.1.5.1.2 When a probe assembly is used to sample a small duct, 30.5 to 91.4 cm (12 to 36 in.) in diameter, the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of  $C_{p(s)}$ . Consult Reference 9 (see Section 17.0) for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 30.5 cm (12 in.) (see Reference 16 in Section 17.0).

#### 10.1.5.2 Recalibration.

10.1.5.2.1 Isolated Pitot Tubes. After each field use, the pitot tube shall be carefully reexamined in top, side, and end views. If the pitot face openings are still aligned within the specifications illustrated in Figure 2-2 and Figure 2-3, it can be assumed that the baseline coefficient of the pitot tube has not changed. If, however,

the tube has been damaged to the extent that it no longer meets the specifications of Figure 2-2 and Figure 2-3, the damage shall either be repaired to restore proper alignment of the face openings, or the tube shall be discarded.

10.1.5.2.2 Pitot Tube Assemblies. After each field use, check the face opening alignment of the pitot tube, as in Section 10.1.5.2.1. Also, remeasure the intercomponent spacings of the assembly. If the intercomponent spacings have not changed and the face opening alignment is acceptable, it can be assumed that the coefficient of the assembly has not changed. If the face opening alignment is no longer within the specifications of Figure 2-2 and Figure 2-3, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the intercomponent spacings have changed, restore the original spacings, or recalibrate the assembly.

10.2 Standard Pitot Tube (if applicable). If a standard pitot tube is used for the velocity traverse, the tube shall be constructed according to the criteria of Section 6.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly, the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

10.3 Temperature Sensors.

10.3.1 After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other sensors at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405°C (761°F), use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference. Alternatively, either a reference thermocouple and potentiometer (calibrated against NIST standards) or thermometric fixed points (e.g., ice bath and boiling water, corrected for barometric pressure) may be used. For temperatures above 405°C (761°F), use a reference thermocouple-potentiometer system calibrated against NIST standards or an alternative reference, subject to the approval of the Administrator.

10.3.2 The temperature data recorded in the field shall be considered valid. If, during calibration, the absolute temperature measured with the sensor being calibrated and the reference sensor agree within 1.5 percent, the temperature data taken in the field shall be considered valid. Otherwise, the pollutant emission test shall either be considered invalid or adjustments (if appropriate) of the test results shall be made, subject to the approval of the Administrator.

10.4 Barometer. Calibrate the barometer used against a mercury barometer.

#### 11.0 Analytical Procedure.

Sample collection and analysis are concurrent for this method (see Section 8.0).

#### 12.0 Data Analysis and Calculations.

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

##### 12.1 Nomenclature.

A = Cross-sectional area of stack,  $\text{m}^2$  ( $\text{ft}^2$ ).

$B_{ws}$  = Water vapor in the gas stream [from Method 4 (reference method) or Method 5], proportion by volume.

$C_p$  = Pitot tube coefficient, dimensionless.

$C_{p(s)}$  = Type S pitot tube coefficient, dimensionless.

$C_{p(std)}$  = Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tube is designed according to the criteria of Sections 6.7.1 to 6.7.5 of this method.

$D_e$  = Equivalent diameter.

K = 0.127 mm  $\text{H}_2\text{O}$  (metric units).  
0.005 in.  $\text{H}_2\text{O}$  (English units).

$K_p$	=	Velocity equation constant.
$L$	=	Length.
$M_d$	=	Molecular weight of stack gas, dry basis (see Section 8.6), g/g-mole (lb/lb-mole).
$M_s$	=	Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).
$n$	=	Total number of traverse points.
$P_{bar}$	=	Barometric pressure at measurement site, mm Hg (in. Hg).
$P_g$	=	Stack static pressure, mm Hg (in. Hg).
$P_s$	=	Absolute stack pressure ( $P_{bar} + P_g$ ), mm Hg (in. Hg),
$P_{std}$	=	Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
$Q_{sd}$	=	Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).
$T$	=	Sensitivity factor for differential pressure gauges.
$T_s$	=	Stack temperature, °C (°F).
$T_{s(abs)}$	=	Absolute stack temperature, °K (°R).
	=	273 + $T_s$ for metric units,
	=	460 + $T_s$ for English units.
$T_{std}$	=	Standard absolute temperature, 293 °K (528 °R).
$v_s$	=	Average stack gas velocity, m/sec (ft/sec).

- W = Width.
- $\sum p$  = Velocity head of stack gas, mm H<sub>2</sub>O (in. H<sub>2</sub>O).
- $\sum p_i$  = Individual velocity head reading at traverse point "i", mm (in.) H<sub>2</sub>O.
- $\sum p_{std}$  = Velocity head measured by the standard pitot tube, cm (in.) H<sub>2</sub>O.
- $\sum p_s$  = Velocity head measured by the Type S pitot tube, cm (in.) H<sub>2</sub>O.
- 3600 = Conversion Factor, sec/hr.
- 18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

12.2 Calculate T as follows:

$$T = \frac{\sum_{i=1}^n \sqrt{p_i + K}}{\sum_{i=1}^n \sqrt{p_i}} \quad \text{Eq. 2-1}$$

12.3 Calculate D<sub>e</sub> as follows:

$$D_e = \frac{2LW}{L+W} \quad \text{Eq. 2-2}$$

12.4 Calibration of Type S Pitot Tube.

12.4.1 For each of the six pairs of  $\sum p$  readings (i.e., three from side A and three from side B) obtained in Section 10.1.3, calculate the value of the Type S pitot tube coefficient according to Equation 2-3:

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{P_{std}}{P}} \quad \text{Eq. 2-3}$$

12.4.2 Calculate  $C_{p(A)}$ , the mean A-side coefficient, and  $C_{p(B)}$ , the mean B-side coefficient. Calculate the difference between these two average values.

12.4.3 Calculate the deviation of each of the three A-side values of  $C_{p(s)}$  from  $C_{p(A)}$ , and the deviation of each of the three B-side values of  $C_{p(s)}$  from  $C_{p(B)}$ , using Equation 2-4:

$$\text{Deviation} = C_{p(s)} - C_{p(A \text{ or } B)} \quad \text{Eq. 2-4}$$

12.4.4 Calculate **F**, the average deviation from the mean, for both the A and B sides of the pitot tube. Use Equation 2-5:

$$F_{A \text{ or } B} = \frac{\sum_{i=1}^3 |C_{p(s)} - \bar{C}_{p(A \text{ or } B)}|}{3} \quad \text{Eq. 2-5}$$

12.5 Molecular Weight of Stack Gas.

$$M_s = M_d (1 - B_{ws}) + 18.0 B_{ws} \quad \text{Eq. 2-6}$$

12.6 Average Stack Gas Velocity.

$$v_s = K_p C_p \sqrt{P_{avg}} \sqrt{\frac{T_{s(abs)}}{P_s M_s}} \quad \text{Eq. 2-7}$$

$$34.97 \frac{\text{m}}{\text{sec}} \left[ \frac{(\text{g/g}\cdot\text{mole})(\text{mmHg})}{(^{\circ}\text{K})(\text{mmH}_2\text{O})} \right]^{\frac{1}{2}} \quad \text{Metric}$$

$$85.49 \frac{\text{m}}{\text{sec}} \left[ \frac{(\text{lb/lb-mole})(\text{in. Hg})}{(^{\circ}\text{R})(\text{in. H}_2\text{O})} \right]^{\frac{1}{2}} \quad \text{English}$$

12.7 Average Stack Gas Dry Volumetric Flow Rate.

$$Q = 3600 (1 - B_{ws}) v_s A \left[ \frac{T_{std} P_s}{T_{s(abs)} P_{std}} \right] \quad \text{Eq. 2-8}$$

13.0 *Method Performance.* [Reserved]

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References.*

1. Mark, L.S. *Mechanical Engineers' Handbook.* New York. McGraw-Hill Book Co., Inc. 1951.

2. Perry, J.H., ed. *Chemical Engineers' Handbook.* New York. McGraw-Hill Book Co., Inc. 1960.

3. Shigehara, R.T., W.F. Todd, and W.S. Smith. *Significance of Errors in Stack Sampling Measurements.* U.S. Environmental Protection Agency, Research Triangle Park, N.C. (Presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, MO., June 14-19, 1970).

4. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Book of ASTM Standards, Part 23. Philadelphia, PA. 1971. ASTM Designation D 2928-71.
5. Vennard, J.K. Elementary Fluid Mechanics. New York. John Wiley and Sons, Inc. 1947.
6. Fluid Meters - Their Theory and Application. American Society of Mechanical Engineers, New York, N.Y. 1959.
7. ASHRAE Handbook of Fundamentals. 1972. p. 208.
8. Annual Book of ASTM Standards, Part 26. 1974. p. 648.
9. Vollaro, R.F. Guidelines for Type S Pitot Tube Calibration. U.S. Environmental Protection Agency, Research Triangle Park, N.C. (Presented at 1st Annual Meeting, Source Evaluation Society, Dayton, OH, September 18, 1975.)
10. Vollaro, R.F. A Type S Pitot Tube Calibration Study. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, N.C. July 1974.
11. Vollaro, R.F. The Effects of Impact Opening Misalignment on the Value of the Type S Pitot Tube Coefficient. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. October 1976.
12. Vollaro, R.F. Establishment of a Baseline Coefficient Value for Properly Constructed Type S Pitot

Tubes. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

13. Vollaro, R.F. An Evaluation of Single-Velocity Calibration Technique as a Means of Determining Type S Pitot Tube Coefficients. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. August 1975.

14. Vollaro, R.F. The Use of Type S Pitot Tubes for the Measurement of Low Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

15. Smith, Marvin L. Velocity Calibration of EPA Type Source Sampling Probe. United Technologies Corporation, Pratt and Whitney Aircraft Division, East Hartford, CT. 1975.

16. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

17. Ower, E. and R.C. Pankhurst. The Measurement of Air Flow, 4th Ed. London, Pergamon Press. 1966.

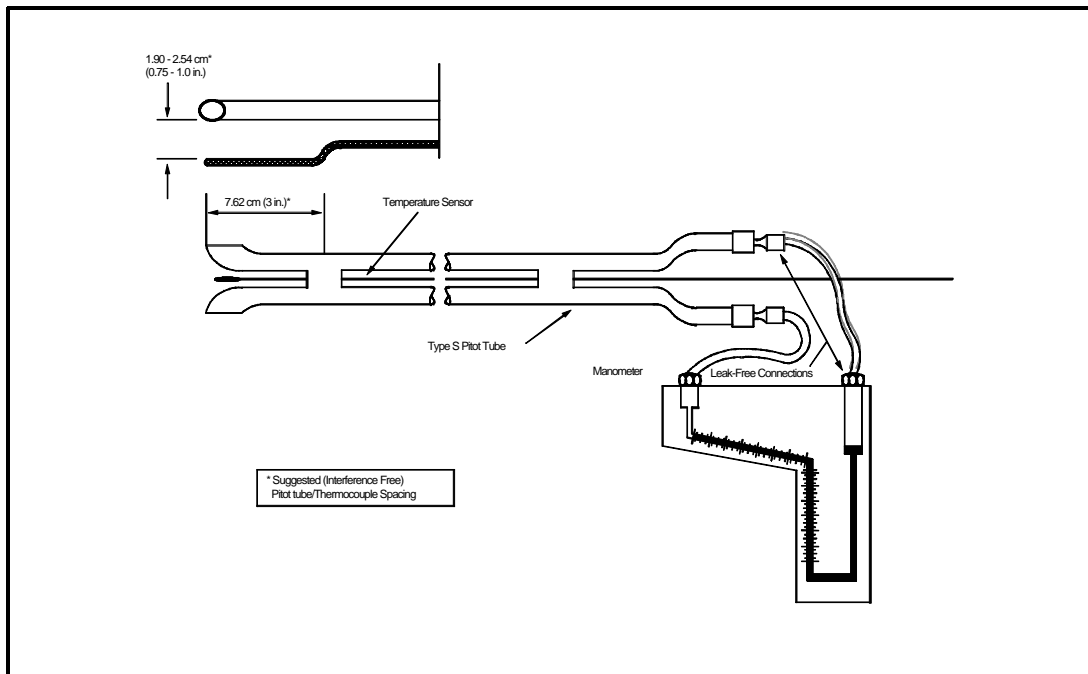
18. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission

Measurement Branch, Research Triangle Park, NC.

November 1976. (Unpublished Paper).

19. Gnyp, A.W., et al. An Experimental Investigation of the Effect of Pitot Tube-Sampling Probe Configurations on the Magnitude of the S Type Pitot Tube Coefficient for Commercially Available Source Sampling Probes. Prepared by the University of Windsor for the Ministry of the Environment, Toronto, Canada. February 1975.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data.*



**Figure 2-1. Type S Pitot Tube Manometer Assembly.**

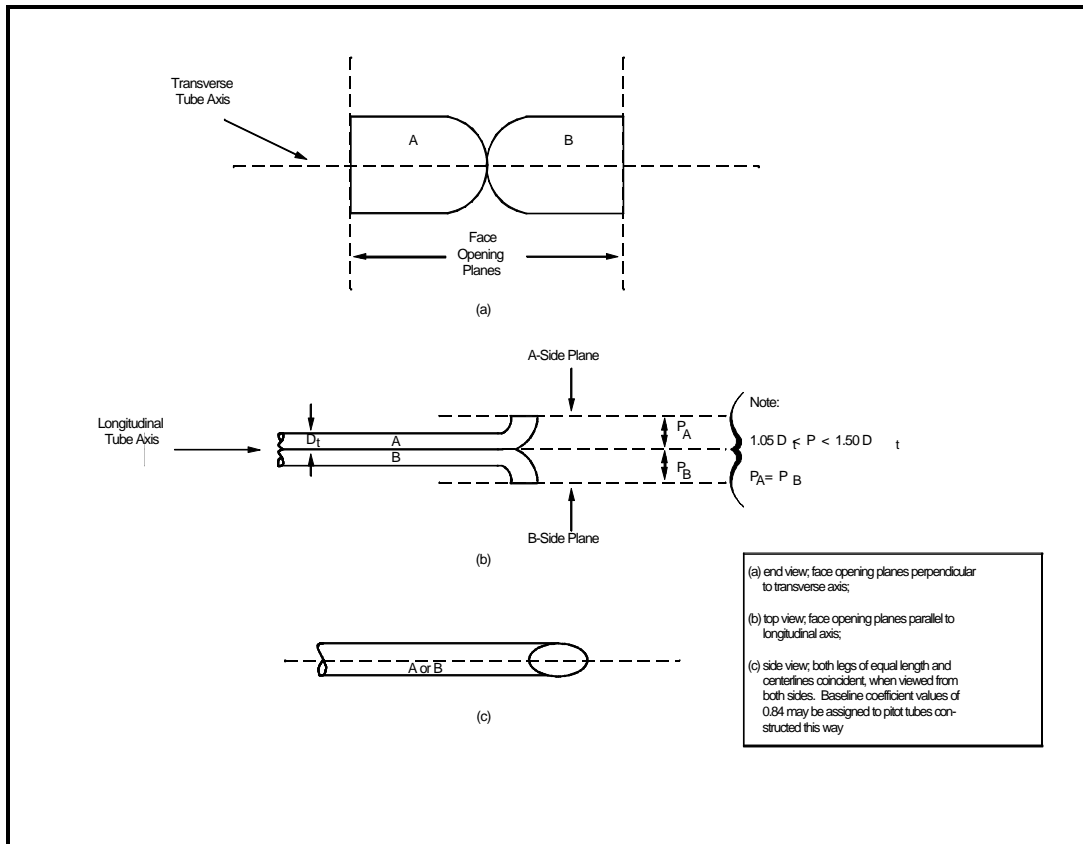
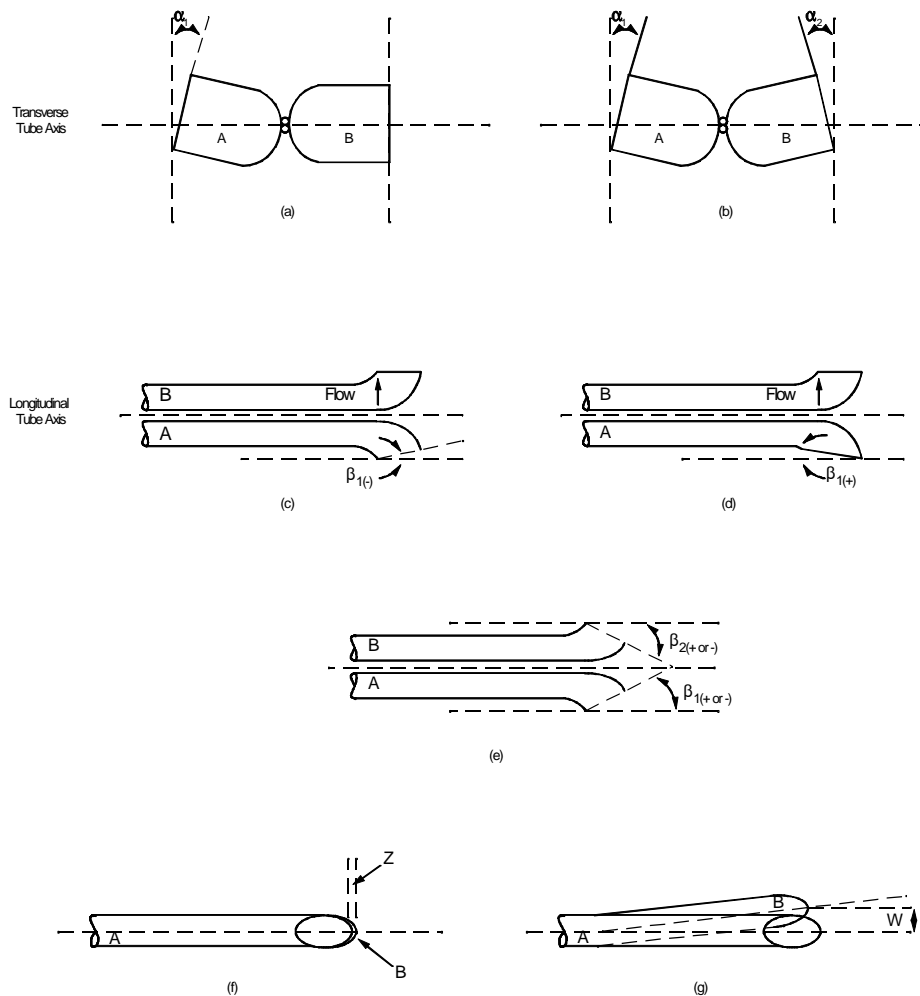
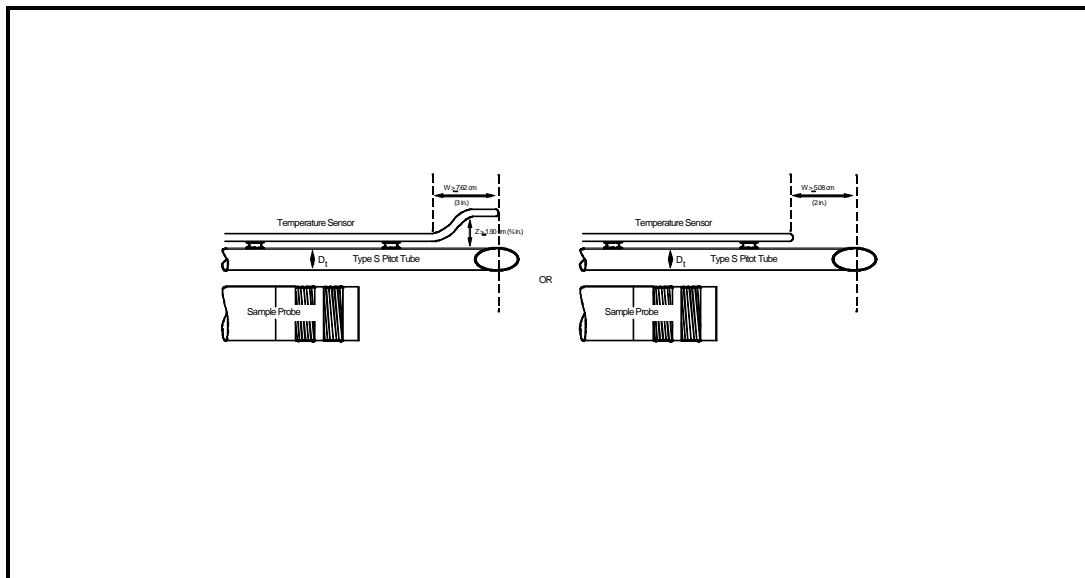


Figure 2-2. Properly Constructed Type S Pitot Tube.



The types of face-opening misalignment shown above will not affect the baseline value of  $C_p(s)$  so long as  $\alpha_1$  and  $\alpha_2 < 0.5^\circ$ ,  $\beta_1$  and  $\beta_2 < 5^\circ$ ,  $z_2 < 0.32 \text{ cm}$  (1/8 in.), and  $w < 0.08 \text{ cm}$  (1/32 in.) (reference 11.0 in Section 16.0).

Figure 2-3. Types of face-opening misalignments that can result from field use or improper construction of type S pitot tubes.



**Figure 2-4. Proper temperature sensor placement to prevent interference;  $D_t$  between 0.48 and 0.95 cm (3/16 and 3/8 in).**

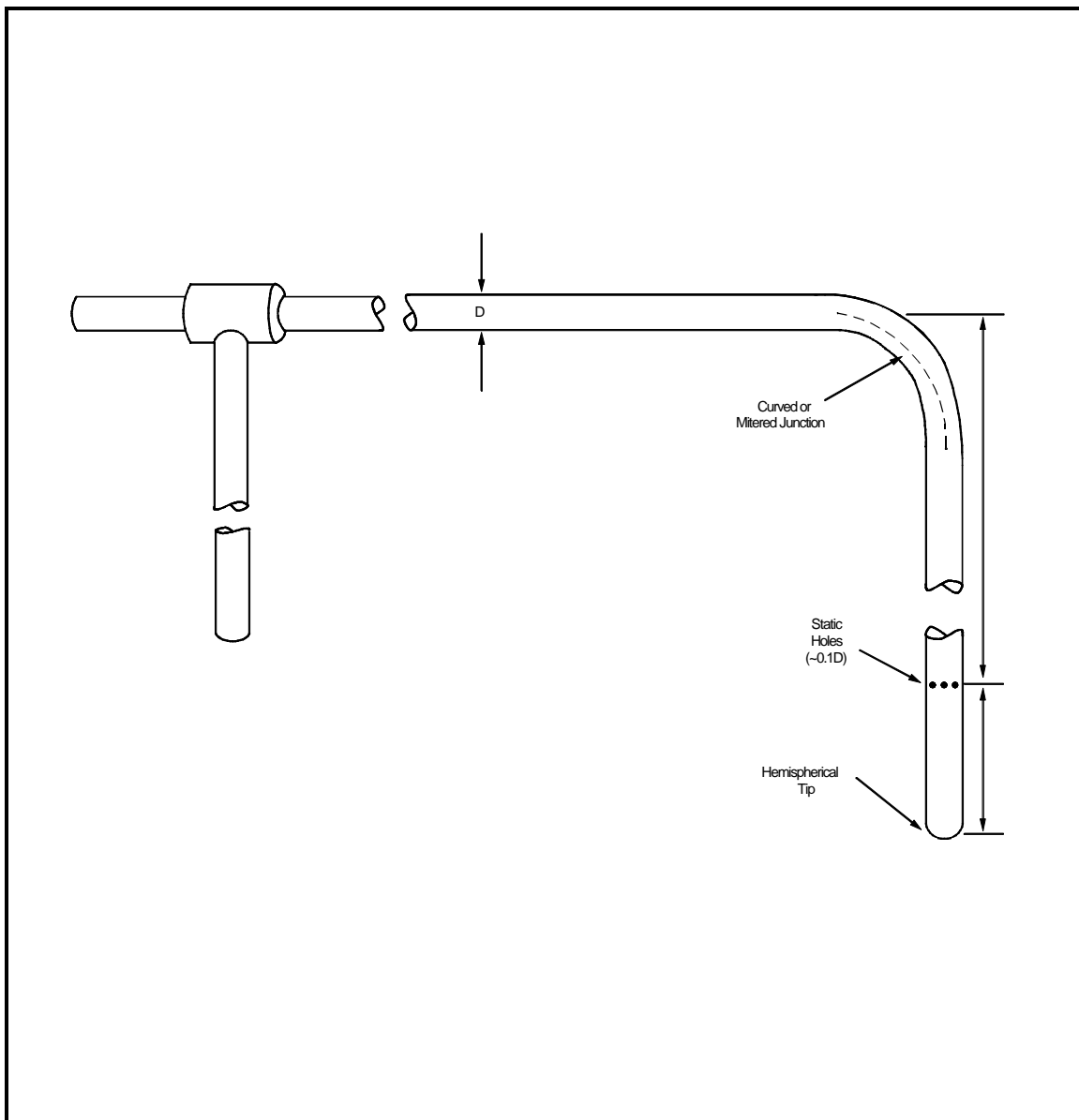


Figure 2-5. Standard pitot tube design specifications.

PLANT \_\_\_\_\_

DATE                      RUN NO.

STACK DIA. OR DIMENSIONS, m (in.) \_\_\_\_\_

BAROMETRIC PRESS., mm Hg (in. Hg) \_\_\_\_\_

CROSS SECTIONAL AREA,  $\text{m}^2$  ( $\text{ft}^2$ ) \_\_\_\_\_

## OPERATORS

PITOT TUBE I.D. NO.

AVG. COEFFICIENT,  $C_p$  = \_\_\_\_\_

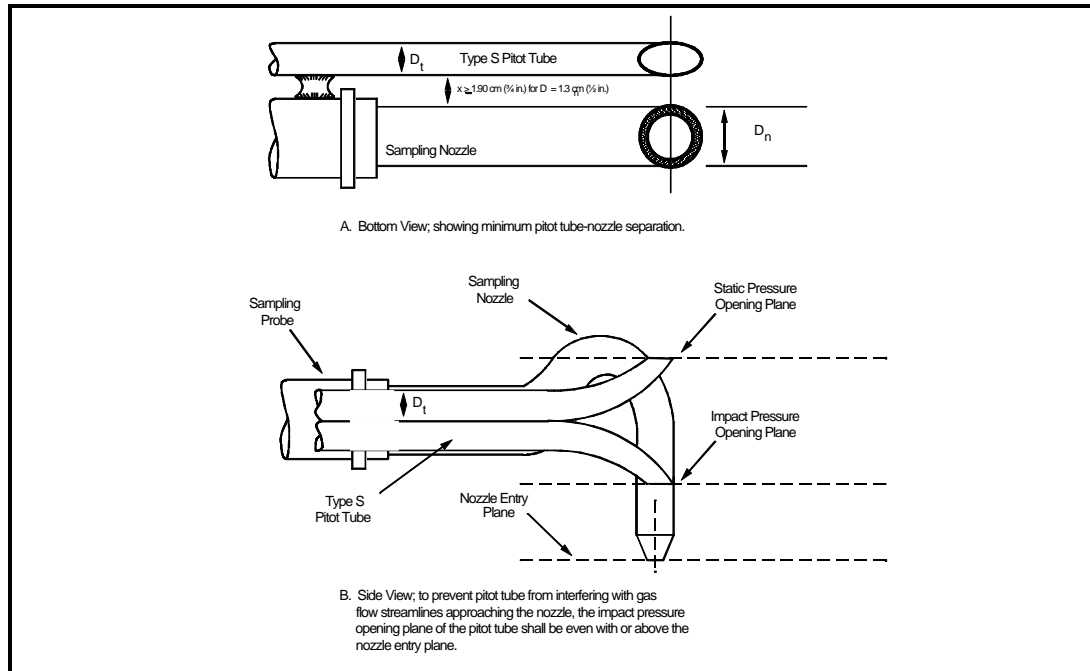
LAST DATE CALIBRATED

### SCHEMATIC OF STACK

## CROSS SECTION

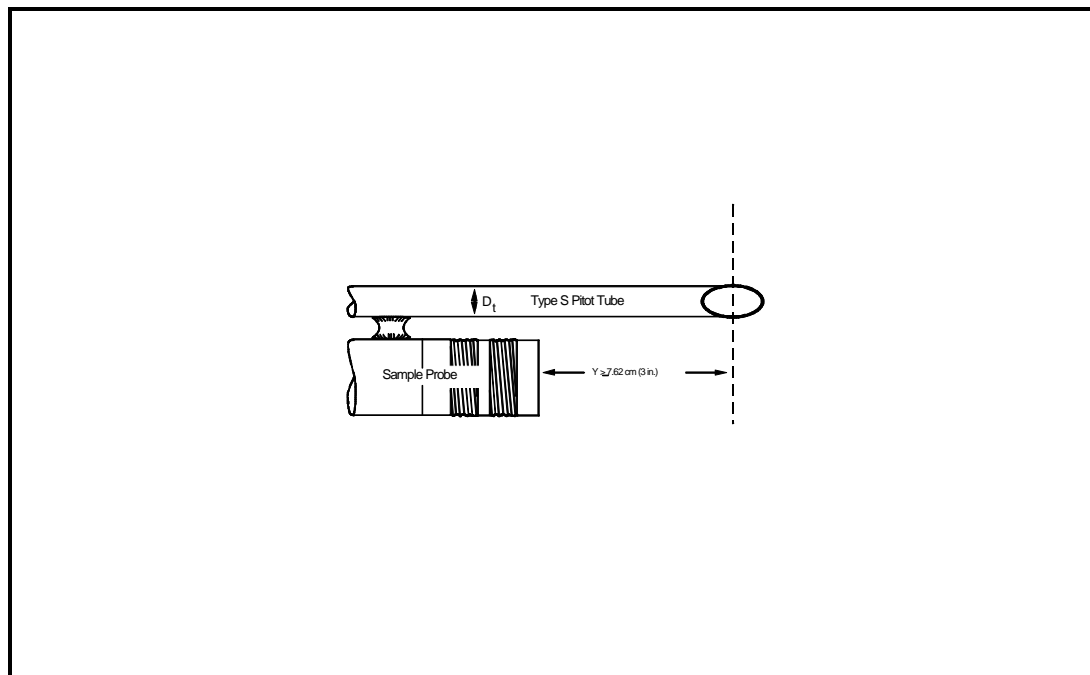
Traverse Pt. No.	Vel. Hd., $\Delta p$ mm (in.) H <sub>2</sub> O	Stack Temperature		$P_g$ mm Hg (in.Hg)	$(\Delta p)^{1/2}$
		T <sub>s</sub> , °C ( °F )	T <sub>s</sub> , °K ( °R )		
Average					

Figure 2-6. Velocity traverse data.



**Figure 2-7. Proper pitot tube-sampling nozzle configuration.**

PITOT TUBE IDENTIFICATION NUMBER: \_\_\_\_\_ DATE: \_\_\_\_\_



**Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference;  $D_t$  between 0.48 and 0.95 cm (3/16 and 3/8 in.).**

CALIBRATED BY: \_\_\_\_\_

"A" SIDE CALIBRATION				
RUN NO.	$\Delta P_{std}$ cm H <sub>2</sub> O (in H <sub>2</sub> O)	$\Delta P_{(s)}$ cm H <sub>2</sub> O (in H <sub>2</sub> O)	$C_{p(s)}$	Deviation $C_{p(s)} - C_p(A)$
1				
2				
3				
		$C_{p,avg}$ (SIDE A)		

"B" SIDE CALIBRATION				
RUN NO.	$\Delta P_{std}$ cm H <sub>2</sub> O (in H <sub>2</sub> O)	$\Delta P_{(s)}$ cm H <sub>2</sub> O (in H <sub>2</sub> O)	$C_{p(s)}$	Deviation $C_{p(s)} - C_p(B)$
1				
2				
3				
		$C_{p,avg}$ (SIDE B)		

$$F_{A \text{ or } B} = \frac{\sum_{i=1}^3 |C_{p(s)} - \bar{C}_{p(A \text{ or } B)}|}{3}$$

Eq. 2-5

[C<sub>p,avg</sub> (side A) - C<sub>p,avg</sub> (side B)] \*

\* Must be less than or equal to 0.01

Figure 2-9. Pitot tube calibration data.

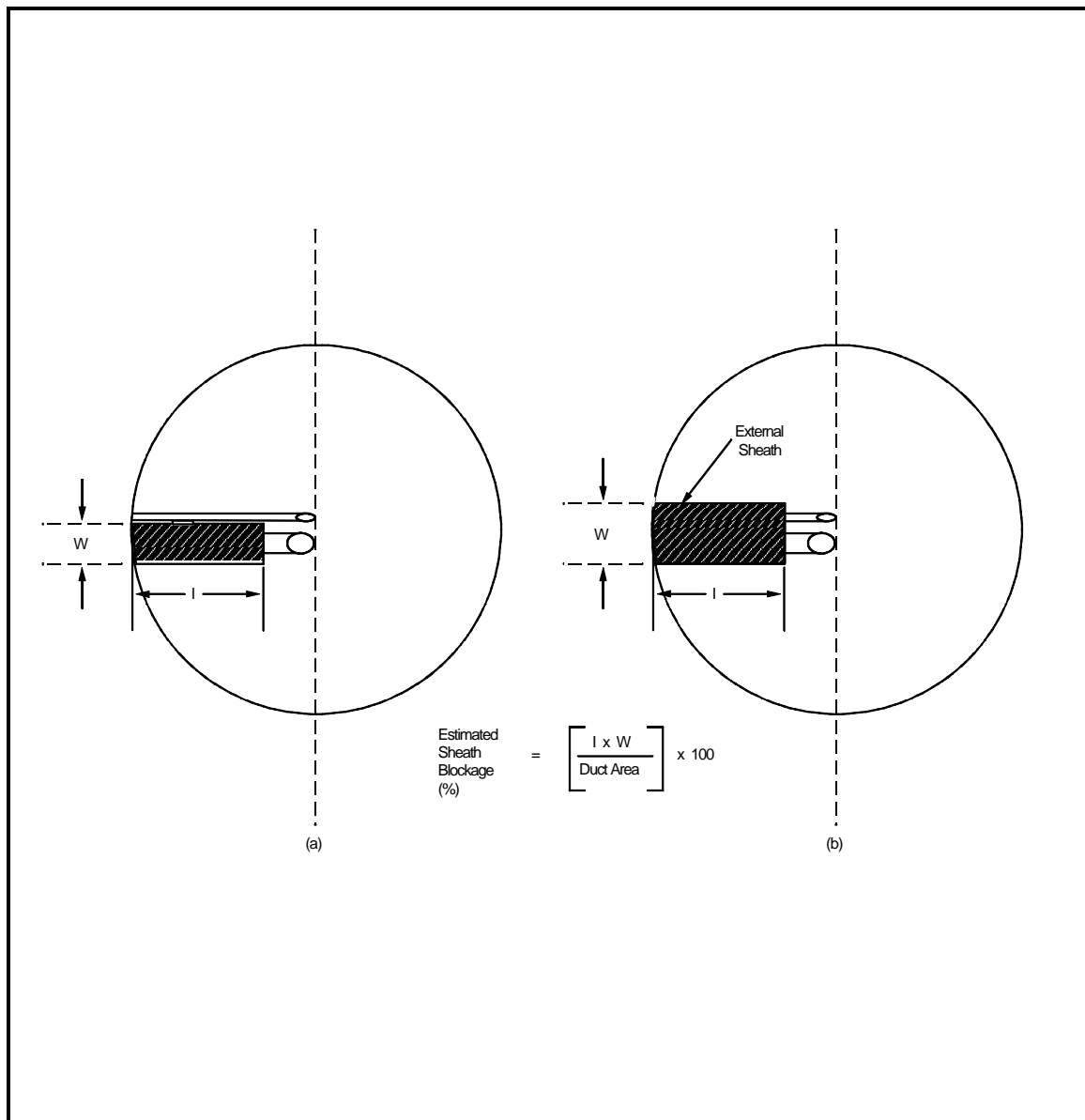


Figure 2-10. Projected-area models for typical pitot tube assemblies

#### METHOD 4 - DETERMINATION OF MOISTURE CONTENT IN STACK GASES

**NOTE:** This method does not include all the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 6.

##### *1.0 Scope and Application.*

##### *1.1 Analytes.*

Analyte	CAS No.	Sensitivity
Water vapor (H <sub>2</sub> O)	7732-18-5	N/A

*1.2 Applicability.* This method is applicable for the determination of the moisture content of stack gas.

*1.3 Data Quality Objectives.* Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

##### *2.0 Summary of Method.*

*2.1* A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

2.2 The method contains two possible procedures: a reference method and an approximation method.

2.2.1 The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data). The approximation method, provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content (e.g., drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc.) are also acceptable.

2.2.2 The reference method is often conducted simultaneously with a pollutant emission measurement run. When it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent. These calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, to be capable of yielding results within one percent H<sub>2</sub>O of the reference method.

3.0 *Definitions.* [Reserved]

#### 4.0 *Interferences.*

4.1 The moisture content of saturated gas streams or streams that contain water droplets, as measured by the reference method, may be positively biased. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows:

Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to  $\pm 1$  °C (2 °F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see Section 8.1.1.1) during the reference method traverse, and calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) using a psychrometric chart and making appropriate corrections if the stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

#### 5.0 *Safety.*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may

not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

#### *6.0 Equipment and Supplies.*

6.1 Reference Method. A schematic of the sampling train used in this reference method is shown in Figure 4-1.

6.1.1 Probe. Stainless steel or glass tubing, sufficiently heated to prevent water condensation, and equipped with a filter, either in-stack (e.g., a plug of glass wool inserted into the end of the probe) or heated out-of-stack (e.g., as described in Method 5), to remove particulate matter. When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

6.1.2 Condenser. Same as Method 5, Section 6.1.1.8.

6.1.3 Cooling System. An ice bath container, crushed ice, and water (or equivalent), to aid in condensing moisture.

6.1.4 Metering System. Same as in Method 5, Section 6.1.1.9, except do not use sampling systems designed for flow rates higher than  $0.0283 \text{ m}^3/\text{min}$  (1.0 cfm). Other metering systems, capable of maintaining a constant sampling

rate to within 10 percent and determining sample gas volume to within 2 percent, may be used, subject to the approval of the Administrator.

6.1.5 Barometer and Graduated Cylinder and/or Balance. Same as Method 5, Sections 6.1.2 and 6.2.5, respectively.

6.2. Approximation Method. A schematic of the sampling train used in this approximation method is shown in Figure 4-2.

6.2.1 Probe. Same as Section 6.1.1.

6.2.2 Condenser. Two midget impingers, each with 30-ml capacity, or equivalent.

6.2.3 Cooling System. Ice bath container, crushed ice, and water, to aid in condensing moisture in impingers.

6.2.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

6.2.5 Valve. Needle valve, to regulate the sample gas flow rate.

6.2.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

6.2.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent,

and calibrated over the range of flow rates and conditions actually encountered during sampling.

6.2.8 Rate Meter. Rotameter, or equivalent, to measure the flow range from 0 to 3 liters/min (0 to 0.11 cfm).

6.2.9 Graduated Cylinder. 25-ml.

6.2.10 Barometer. Same as Method 5, Section 6.1.2.

6.2.11 Vacuum Gauge. At least 760-mm (30-in.) Hg gauge, to be used for the sampling leak check.

7.0 *Reagents and Standards.* [Reserved]

8.0 *Sample Collection, Preservation, Transport, and Storage.*

8.1 Reference Method. The following procedure is intended for a condenser system (such as the impinger system described in Section 6.1.1.8 of Method 5) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

8.1.1 Preliminary Determinations.

8.1.1.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than

0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.1.1.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m<sup>3</sup>/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

#### 8.1.2 Preparation of Sampling Train.

8.1.2.1 Place known volumes of water in the first two impingers; alternatively, transfer water into the first two impingers and record the weight of each impinger (plus water) to the nearest 0.5 g. Weigh and record the weight of

the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

8.1.2.2 Set up the sampling train as shown in Figure 4-1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of approximately 120 °C (248 °F), to prevent water condensation ahead of the condenser. Allow time for the temperatures to stabilize. Place crushed ice and water in the ice bath container.

8.1.3 Leak Check Procedures. It is recommended, but not required, that the volume metering system and sampling train be leak-checked as follows:

8.1.3.1 Metering System. Same as Method 5, Section 8.4.1.

8.1.3.2 Sampling Train. Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder), and pull a 380 mm (15 in.) Hg vacuum. A lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m<sup>3</sup>/min (0.020 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

8.1.4 Sampling Train Operation. During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on a data sheet similar to that shown in Figure 4-3. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point at least once during each time increment.

**NOTE:** When Method 4 is used concurrently with an isokinetic method (e.g., Method 5) the sampling rate should be maintained at isokinetic conditions rather than 10 percent of constant rate.

8.1.4.1 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump, and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the silica gel outlet.

8.1.4.2 After collecting the sample, disconnect the probe from the first impinger (or from the filter holder), and conduct a leak check (mandatory) of the sampling train as described in Section 8.1.3.2. Record the leak rate. If

the leakage rate exceeds the allowable rate, either reject the test results or correct the sample volume as in Section 12.3 of Method 5.

## 8.2 Approximation Method.

**NOTE:** The approximation method described below is presented only as a suggested method (see Section 2.0).

8.2.1 Place exactly 5 ml water in each impinger. Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet. Then, plug the probe inlet and pull a vacuum of at least 250 mm (10 in.) Hg. Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0 to 40 ml/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

**NOTE:** Release the probe inlet plug slowly before turning off the pump.

8.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 liters/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft<sup>3</sup>) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as indicated by Figure 4-4.



## 9.0 *Quality Control.*

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
Section 8.1.1.4	Leak rate of the sampling system cannot exceed four percent of the average sampling rate or 0.00057 m <sup>3</sup> /min (0.20 cfm).	Ensures the accuracy of the volume of gas sampled. (Reference Method)
Section 8.2.1	Leak rate of the sampling system cannot exceed two percent of the average sampling rate.	Ensures the accuracy of the volume of gas sampled. (Approximation Method)

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 *Calibration and Standardization.*

**NOTE:** Maintain a laboratory log of all calibrations.

10.1 Reference Method. Calibrate the metering system, temperature sensors, and barometer according to Method 5, Sections 10.3, 10.5, and 10.6, respectively.

10.2 Approximation Method. Calibrate the metering system and the barometer according to Method 6, Section 10.1 and Method 5, Section 10.6, respectively.

## 11.0 *Analytical Procedure.*

11.1 Reference Method. Measure the volume of the moisture condensed in each of the impingers to the nearest

ml. Alternatively, if the impingers were weighed prior to sampling, weigh the impingers after sampling and record the difference in weight to the nearest 0.5 g. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4-5), and calculate the moisture content, as described in Section 12.0.

11.2 Approximation Method. Combine the contents of the two impingers, and measure the volume to the nearest 0.5 ml.

## *12.0 Data Analysis and Calculations.*

Carry out the following calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

### 12.1 Reference Method

#### 12.1.1 Nomenclature.

$B_{ws}$  = Proportion of water vapor, by volume, in the gas stream.

$M_w$  = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

$P_m$  = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

$P_{std}$  = Standard absolute pressure, 760 mm Hg

(29.92 in. Hg).

$R$  = Ideal gas constant,  
0.06236 (mm Hg)(m<sup>3</sup>)/(g-mole)(°K) for metric  
units and 21.85 (in. Hg)(ft<sup>3</sup>)/(lb-mole)(°R)  
for English units.

$T_m$  = Absolute temperature at meter, °K (°R).

$T_{std}$  = Standard absolute temperature, 293 °K  
(528 °R).

$V_f$  = Final volume of condenser water, ml.

$V_i$  = Initial volume, if any, of condenser water,  
ml.

$V_m$  = Dry gas volume measured by dry gas meter, dcm  
(dcf).

$V_{m(std)}$  = Dry gas volume measured by the dry gas meter,  
corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$  = Volume of water vapor condensed, corrected to  
standard conditions, scm (scf).

$V_{wsg(std)}$  = Volume of water vapor collected in silica gel,  
corrected to standard conditions, scm (scf).

$W_f$  = Final weight of silica gel or silica gel plus  
impinger, g.

$W_i$  = Initial weight of silica gel or silica gel  
plus impinger, g.

$Y$  = Dry gas meter calibration factor.

$\Delta V_m$  = Incremental dry gas volume measured by dry gas

meter at each traverse point, dcm (dcf).

$D_w$  = Density of water, 0.9982 g/ml  
(0.002201 lb/ml).

#### 12.1.1.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i) \rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1 (V_f - V_i)$$

**Eq. 4-1**

where:

$K_1$  = 0.001333 m<sup>3</sup>/ml for metric units,  
= 0.04706 ft<sup>3</sup>/ml for English units.

#### 12.1.1.3 Volume of Water Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w K_2}$$

$$= K_3 (W_f - W_i)$$

**Eq. 4-2**

where:

$K_2$  = 1.0 g/g for metric units  
= 453.6 g/lb for English units  
 $K_3$  = 0.001335 m<sup>3</sup>/g for metric units,  
= 0.04715 ft<sup>3</sup>/g for English units.

#### 12.1.1.4 Sample Gas Volume.

$$\begin{aligned}
 V_{m(\text{std})} &= \frac{V_m Y P_m T_{\text{std}}}{P_{\text{std}} T_m} \\
 &= K_4 Y \frac{V_m P_m}{T_m}
 \end{aligned}
 \tag{Eq. 4-3}$$

where:

$K_4$  = 0.3855 °K/mm Hg for metric units,  
 = 17.64 °R/in. Hg for English units.

**NOTE:** If the post-test leak rate (Section 8.1.4.2) exceeds the allowable rate, correct the value of  $V_m$  in Equation 4-3, as described in Section 12.3 of Method 5.

#### 12.1.1.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(\text{std})} + V_{wsg(\text{std})}}{V_{wc(\text{std})} + V_{wsg(\text{std})} + V_{m(\text{std})}}
 \tag{Eq. 4-4}$$

12.1.1.6 Verification of Constant Sampling Rate. For each time increment, determine the  $V_m$ . Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results, and repeat the run.

12.1.1.7 In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the

saturated conditions (see Section 4.1), and another based upon the results of the impinger analysis. The lower of these two values of  $B_{ws}$  shall be considered correct.

12.2 Approximation Method. The approximation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

#### 12.2.1 Nomenclature.

- $B_{wm}$  = Approximate proportion by volume of water vapor in the gas stream leaving the second impinger, 0.025.
- $B_{ws}$  = Water vapor in the gas stream, proportion by volume.
- $M_w$  = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- $P_m$  = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).
- $P_{std}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- $R$  = Ideal gas constant,  
0.06236 [(mm Hg)(m<sup>3</sup>)]/[(g-mole)(K)]

for metric units and

21.85 [(in. Hg)(ft<sup>3</sup>)]/[(lb-mole)(°R)] for

English units.

$T_m$  = Absolute temperature at meter, °K (°R).

$T_{std}$  = Standard absolute temperature, 293 °K  
(528 °R).

$V_f$  = Final volume of impinger contents, ml.

$V_i$  = Initial volume of impinger contents, ml.

$V_m$  = Dry gas volume measured by dry gas meter,  
dcm (dcf).

$V_{m(std)}$  = Dry gas volume measured by dry gas meter,  
corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$  = Volume of water vapor condensed, corrected to  
standard conditions, scm (scf).

$Y$  = Dry gas meter calibration factor.

$D_w$  = Density of water, 0.09982 g/ml  
(0.002201 lb/ml).

#### 12.2.2 Volume of Water Vapor Collected.

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_5 (V_f - V_i)$$

**Eq. 4-5**

where:

$K_5$  = 0.001333 m<sup>3</sup>/ml for metric units,  
= 0.04706 ft<sup>3</sup>/ml for English units.

## 12.2.3 Sample Gas Volume.

$$\begin{aligned}
 V_{m(\text{std})} &= \frac{V_m Y P_m T_{\text{std}}}{P_{\text{std}} T_m} \\
 &= K_6 Y \frac{V_m P_m}{T_m}
 \end{aligned}
 \tag{Eq. 4-6}$$

where:

$$\begin{aligned}
 K_6 &= 0.3855 \text{ } ^\circ\text{K/mm Hg for metric units,} \\
 &= 17.64 \text{ } ^\circ\text{R/in. Hg for English units.}
 \end{aligned}$$

## 12.2.4 Approximate Moisture Content.

$$\begin{aligned}
 B_{ws} &= \frac{V_{wc(\text{std})}}{V_{wc(\text{std})} + V_{m(\text{std})}} + B_{wm} \\
 &= \frac{V_{wc(\text{std})}}{V_{wc(\text{std})} + V_{m(\text{std})}} + (0.025)
 \end{aligned}
 \tag{Eq. 4-7}$$

13.0 *Method Performance.* [Reserved]

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *Alternative Procedures.*

The procedure described in Method 5 for determining moisture content is acceptable as a reference method.

17.0 *References.*

1. Air Pollution Engineering Manual (Second Edition).  
Danielson, J.A. (ed.). U.S. Environmental Protection

Agency, Office of Air Quality Planning and Standards.  
Research Triangle Park, NC. Publication No. AP-40. 1973.

2. Devorkin, Howard, et al. Air Pollution Source  
Testing Manual. Air Pollution Control District, Los  
Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust  
and Mist Content of Gases. Western Precipitation Division  
of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP-50.  
1968.

*18.0 Tables, Diagrams, Flowcharts, and Validation Data.*

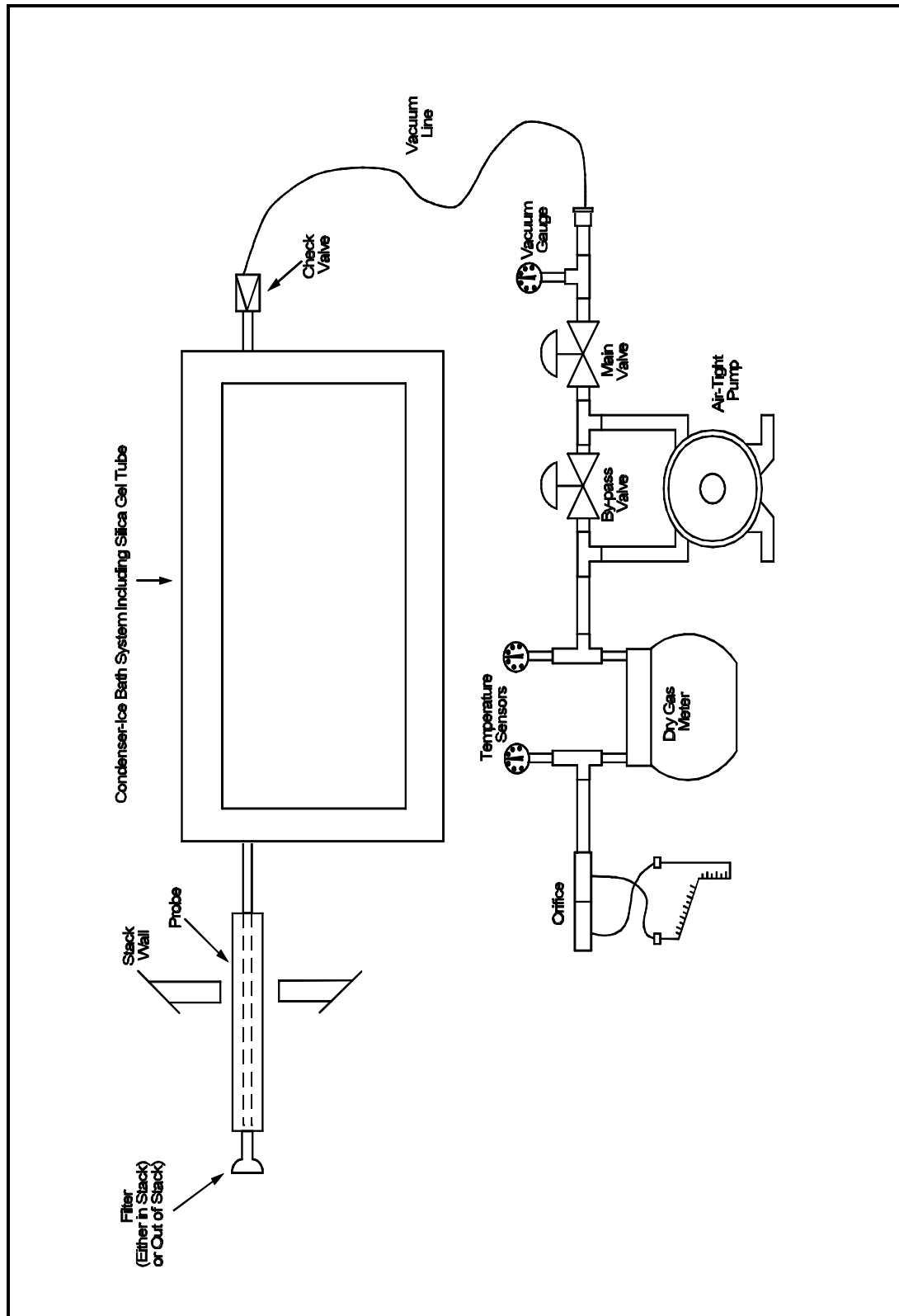


Figure 4-1. Moisture Sampling Train-Reference Method

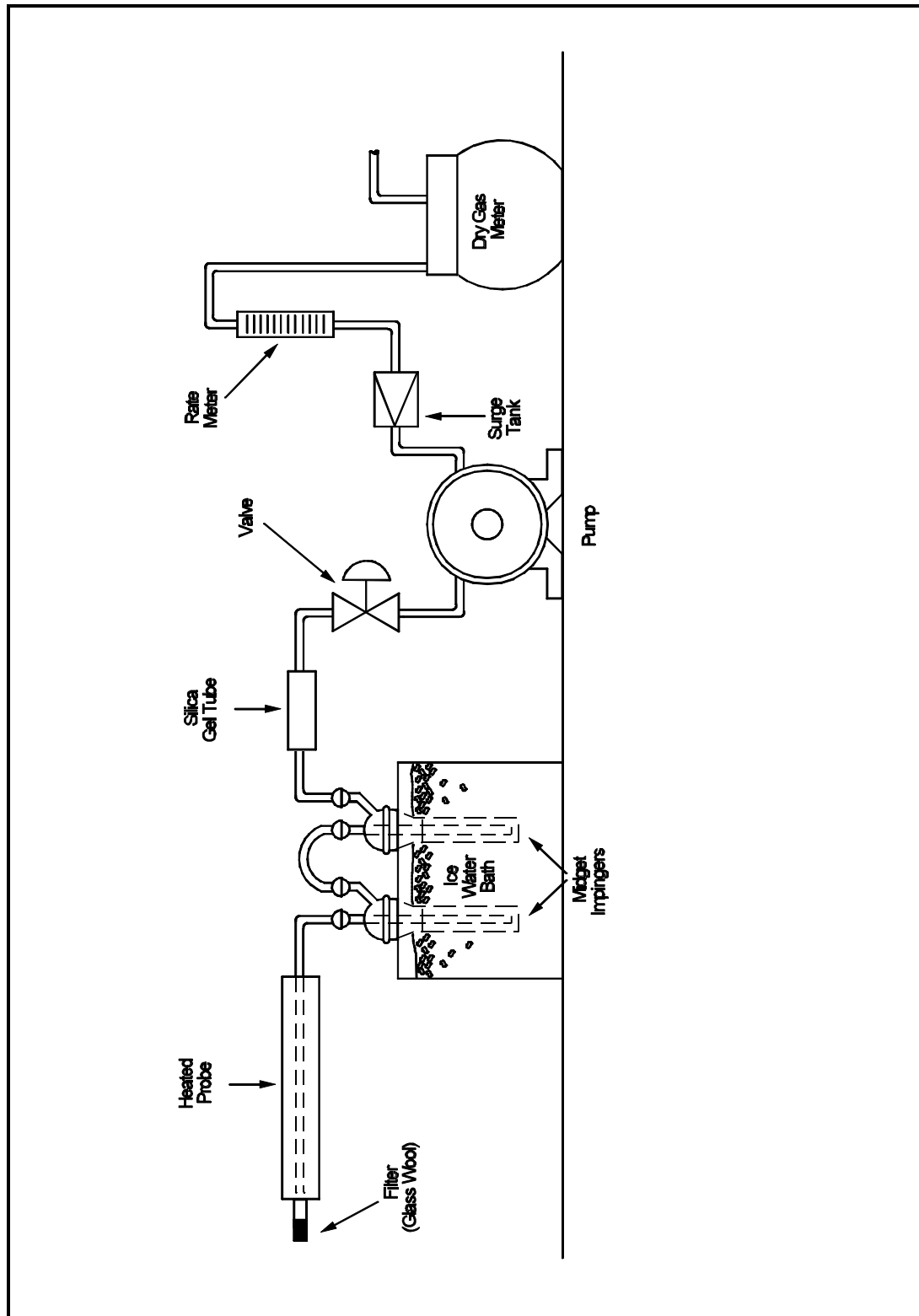
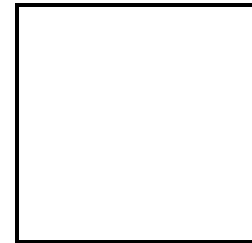


Figure 4-2. Moisture Sampling Train - Approximation Method.

Plant \_\_\_\_\_  
 Location \_\_\_\_\_  
 Operator \_\_\_\_\_  
 Date \_\_\_\_\_  
 Run No. \_\_\_\_\_  
 Ambient temperature \_\_\_\_\_  
 Barometric pressure \_\_\_\_\_  
 Probe Length \_\_\_\_\_



SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Sampling Time (1), min	Stack Temperature °C (°F)	Pressure differential across orifice meter )H mm (in.) H <sub>2</sub> O	Meter Reading gas sample volume m <sup>3</sup> (ft <sup>3</sup> )	)V <sub>m</sub> m <sup>3</sup> (ft <sup>3</sup> )	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet T <sub>m_in</sub> °C (°F)	Outlet T <sub>m_out</sub> °C (°F)	
Average								

Figure 4-3. Moisture Determination. - Reference Method

Location \_\_\_\_\_ Comments: \_\_\_\_\_  
 Test \_\_\_\_\_  
 Date \_\_\_\_\_  
 Operator \_\_\_\_\_  
 Barometric pressure \_\_\_\_\_

Clock Time	Gas volume through meter, ( $V_m$ ), $m^3$ ( $ft^3$ )	Rate meter setting $m^3/min$ ( $ft^3/min$ )	Meter temperature $^{\circ}C$ ( $^{\circ}F$ )

**Figure 4-4. Example Moisture Determination Field Data Sheet - Approximation Method.**

	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Difference		

**Figure 4-5. Analytical Data - Reference Method.**

**METHOD 5 - DETERMINATION OF PARTICULATE MATTER  
EMISSIONS FROM STATIONARY SOURCES**

**NOTE:** This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

*1.0 Scope and Application.*

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of PM emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

*2.0 Summary of Method.*

Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature of  $120 \pm 14^{\circ}\text{C}$  ( $248 \pm 25^{\circ}\text{F}$ ) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that

condenses at or above the filtration temperature, is determined gravimetrically after the removal of uncombined water.

3.0 *Definitions.* [Reserved]

4.0 *Interferences.* [Reserved]

5.0 *Safety.*

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 *Equipment and Supplies.*

6.1 *Sample Collection.* The following items are required for sample collection:

6.1.1 *Sampling Train.* A schematic of the sampling train used in this method is shown in Figure 5-1 in Section 18.0. Complete construction details are given in APTD-0581 (Reference 2 in Section 17.0); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

**NOTE:** The operating and maintenance procedures for the sampling train are described in APTD-0576 (Reference 3 in Section 17.0). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

6.1.1.1 Probe Nozzle. Stainless steel (316) or glass with a sharp, tapered leading edge. The angle of taper shall be  $\leq 30^\circ$ , and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm (1/8 to 1/2 in) inside diameter (ID) in increments of 0.16 cm (1/16 in). Larger nozzle sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated, according to the procedures outlined in Section 10.1.

6.1.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe

gas temperature during sampling of  $120 \pm 14$  °C ( $248 \pm 25$  °F), or such other temperature as specified by an applicable subpart of the standards or as approved by the Administrator for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F); quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1,650 °F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820 °C (1500°F), and for quartz glass it is 1500 °C (2700 °F). Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

6.1.1.3 Pitot Tube. Type S, as described in Section 6.1 of Method 2, or other device approved by the

Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-7) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 10.0 of Method 2.

6.1.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 6.2 of Method 2. One manometer shall be used for velocity head ( $\rho$ ) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder of  $120 \pm 14$  °C ( $248 \pm 25$  °F) during sampling, or such

other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.1.7 Temperature Sensor. A temperature sensor capable of measuring temperature to within  $\pm 3$  °C (5.4 °F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas, and the temperature around the filter holder can be regulated and monitored during sampling.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm ( $\frac{1}{2}$  in.) ID glass tube extending to about 1.3 cm ( $\frac{1}{2}$  in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 8.3.1), the third shall

be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A temperature sensor, capable of measuring temperature to within 1 °C (2 °F) shall be placed at the outlet of the fourth impinger for monitoring purposes. Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. An acceptable technique involves the measurement of condensed water either gravimetrically or volumetrically and the determination of the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 °C (68 °F) and determining the weight gain. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

**NOTE:** If a determination of the PM collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

6.1.1.9 Metering System. Vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature to within 3 °C (5.4 °F), dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1 10 Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in.).

**NOTE:** The barometric pressure reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm Hg (0.1 in.) per 30 m (100 ft) elevation increase or plus 2.5 mm Hg (0.1 in) per 30 m (100 ft) elevation decrease.

#### 6.1.3 Gas Density Determination Equipment.

Temperature sensor and pressure gauge, as described in Sections 6.3 and 6.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-4). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube.

(This alternative is subject to the approval of the Administrator.)

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash Bottles. Two Glass wash bottles are recommended. Alternatively, polyethylene wash bottles may be used. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

6.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml.

6.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

6.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample Analysis. The following equipment is required for sample analysis:

6.3.1 Glass Weighing Dishes.

6.3.2 Desiccator.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature Sensor. To measure the temperature of the laboratory environment.

7.0 *Reagents and Standards.*

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency ( $<0.05$  percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986-71, 78, or 95a (incorporated by reference - see §60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing  $\text{SO}_2$  or  $\text{SO}_3$ , the filter material must be of a type that is unreactive to  $\text{SO}_2$  or  $\text{SO}_3$ . Reference 10 in Section 17.0 may be used to select the appropriate filter.

7.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at  $175\text{ }^{\circ}\text{C}$  ( $350\text{ }^{\circ}\text{F}$ ) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water [to conform to ASTM D 1193-77 or 91 Type 3 (incorporated by reference - see §60.17)] shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed Ice.

7.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

7.2 Sample Recovery. Acetone, reagent grade,  $\leq 0.001$  percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values ( $\leq 0.001$  percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

7.3 Sample Analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in Section 7.2.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

*8.0 Sample Collection, Preservation, Storage, and Transport.*

8.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD-0576.

8.1.1 Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 Check filters visually against light for irregularities, flaws, or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or polyethylene petri dishes), and keep each filter in its identified container at all times except during sampling.

8.1.3 Desiccate the filters at  $20 \pm 5.6$  °C ( $68 \pm 10$  °F) and ambient pressure for at least 24 hours. Weigh each filter (or filter and shipping container) at intervals of at least 6 hours to a constant weight (*i.e.*,  $\leq 0.5$  mg change from previous weighing). Record results to the nearest 0.1 mg. During each weighing, the period for which the filter is exposed to the laboratory atmosphere shall be less than 2 minutes. Alternatively (unless otherwise specified

by the Administrator), the filters may be oven dried at 105 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

## 8.2 Preliminary Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the pitot lines (see Method 2, Section 8.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 8.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the

range of velocity heads encountered (see Section 8.3 of Method 2).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

8.2.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

### 8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) or a heat-resistant string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used.

When metal liners are used, install the nozzle as discussed above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid the possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

#### 8.4 Leak-Check Procedures.

8.4.1 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-2): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of

the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest Leak Check. A pretest leak check of the sampling train is recommended, but not required. If the pretest leak check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

**NOTE:** A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If a heat-resistant string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380

mm (15 in.) Hg vacuum (see **NOTE** in Section 8.4.2.1). Then connect the probe to the train, and leak-check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m<sup>3</sup>/min (0.020 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum, or end the leak check and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable), and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the

silica gel from being entrained backward into the third impinger.

8.4.3 Leak Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in Section 8.4.2 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than  $0.00057 \text{ m}^3/\text{min}$  (0.020 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in Section 12.3 of this method, or void the sample run.

**NOTE:** Immediately after component changes, leak checks are optional. If such leak checks are done, the procedure outlined in Section 8.4.2 above should be used.

8.4.4 Post-Test Leak Check. A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in

accordance with the procedures outlined in Section 8.4.2, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than  $0.00057 \text{ m}^3/\text{min}$  ( $0.020 \text{ cfm}$ ) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume as shown in Section 12.3 of this method, or void the sampling run.

8.5 Sampling Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of  $120 \pm 14 \text{ }^\circ\text{C}$  ( $248 \pm 25 \text{ }^\circ\text{F}$ ), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5-3. Be sure to record the initial DGM reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure 5-3 at least once at each sample point

during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of collecting deposited material. To begin sampling, verify that the filter and probe heating systems are up to temperature, remove the nozzle cap, verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump, and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient ( $C_p$ ) is  $0.85 \pm 0.02$ , and the stack gas equivalent density [dry molecular weight ( $M_d$ )] is equal to  $29 \pm 4$ . APTD-0576 details the procedure for using the nomographs. If  $C_p$  and  $M_d$  are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 7 in Section 17.0) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (*i.e.*, height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run.

It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see Section 8.4.3). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

**NOTE:** When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

8.5.9 At the end of the sample run, close the coarse adjust valve, remove the probe and nozzle from the stack,

turn off the pump, record the final DGM meter reading, and conduct a post-test leak check, as outlined in Section 8.4.4. Also, leak-check the pitot lines as described in Method 2, Section 8.1. The lines must pass this leak check, in order to validate the velocity head data.

8.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 12.11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Administrator for possible variance on the isokinetic rates.

#### 8.7 Sample Recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thereby drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the

silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened, and cap it. Remove the umbilical cord from the last impinger, and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder, and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used, and place it in a glass sample container labeled "acetone blank."

8.7.6 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri

dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry Nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Deionized distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator. In these cases, save a water blank, and follow the Administrator's directions on analysis. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle. Clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to allow determination of whether leakage occurred during transport. Label the container to identify clearly its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of

dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in Section 11.2.3.

8.7.6.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see **NOTE**, Section 6.1.1.8). If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

8.8 Sample Transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

## 9.0 *Quality Control.*

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
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8.4, 10.1-10.6	Sampling equipment leak check and calibration	Ensures accurate measurement of stack gas flow rate, sample volume
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9.2 Volume Metering System Checks. The following procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 10.3, determine the  $\Delta H_o$  for the metering system orifice. The  $\Delta H_o$  is the orifice pressure differential in units of in. H<sub>2</sub>O that correlates to 0.75 cfm of air at

$$\Delta H_o = 0.0319 \Delta H \frac{T_M Z^2}{P_{bar} Y^2 V_m^2}$$

528 °R and 29.92 in. Hg. The  $\Delta H_o$  is calculated as follows:where:

$\Delta H$  = Average pressure differential across the orifice meter, in. H<sub>2</sub>O.

$T_m$  = Absolute average DGM temperature, °R.

$P_{bar}$  = Barometric pressure, in. Hg.

$Z$  = Total sampling time, min.

$Y$  = DGM calibration factor, dimensionless.

$V_m$  = Volume of gas sample as measured by DGM, dcf.

$$0.0319 = (0.0567 \text{ in. Hg/}^\circ\text{R})(0.75 \text{ cfm})^2$$

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (*i.e.*, pump, volume meter, and orifice) at the  $H_0$  pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value,  $Y_c$ , as follows:

$$Y_c = \frac{10}{V_m} \left[ \frac{0.0319 T_m}{P_{bar}} \right]^{\frac{1}{2}}$$

where:

$Y_c$  = DGM calibration check value, dimensionless.

10 = Run time, min.

9.2.1.2 Compare the  $Y_c$  value with the dry gas meter calibration factor  $Y$  to determine that:  $0.97Y < Y_c < 1.03Y$ . If the  $Y_c$  value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated Critical Orifice. A critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a check by following the procedure of Section 16.2.

*10.0 Calibration and Standardization.*

**NOTE:** Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 10.1 of Method 2.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5-4. The wet test meter should have a capacity of 30 liters/rev (1 ft<sup>3</sup>/rev). A spirometer of 400 liters (14 ft<sup>3</sup>) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically

calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of  $0.14 \text{ m}^3$  ( $5 \text{ ft}^3$ ) at all orifice settings. Record all the data on a form similar to Figure 5-5 and calculate  $Y$ , the DGM calibration factor, and  $H_o$ , the orifice calibration factor, at each orifice setting as shown on Figure 5-5. Allowable tolerances for individual  $Y$  and  $H_o$  values are given in Figure 5-5. Use the average of the  $Y$  values in the calculations in Section 12.0.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak-check

procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at  $0.00057 \text{ m}^3/\text{min}$  ( $0.020 \text{ cfm}$ ). At the end of the run, take the difference of the measured wet test meter and DGM volumes. Divide the difference by 10 to get the leak rate. The leak rate should not exceed  $0.00057 \text{ m}^3/\text{min}$  ( $0.020 \text{ cfm}$ ).

10.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as detailed in Section 10.3.1.

**NOTE:** Alternative procedures (e.g., rechecking the orifice meter coefficient) may be used, subject to the approval of the Administrator.

10.3.3 Acceptable Variation in Calibration. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall

either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (*i.e.*, before or after) gives the lower value of total sample volume.

10.4 Probe Heater Calibration. Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

**NOTE:** The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature Sensors. Use the procedure in Section 10.3 of Method 2 to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

10.6 Barometer. Calibrate against a mercury barometer.

*11.0 Analytical Procedure.*

11.1 Record the data required on a sheet such as the one shown in Figure 5-6.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight, and report the results to the nearest 0.1 mg. For the purposes of this section, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings. Alternatively, the sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The sample may be oven dried at 104 °C (220 °F) for 2 to 3 hours. Once the sample has cooled, weigh the sample, and use this weight as a final weight.

11.2.2 Container No. 2. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to  $\pm 1$  ml or gravimetrically to  $\pm 0.5$  g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Acetone Blank Container. Measure the acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

**NOTE:** The contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point

of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

#### 12.0 Data Analysis and Calculations.

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used, provided that they give equivalent results.

##### 12.1 Nomenclature.

- $A_n$  = Cross-sectional area of nozzle,  $m^2$  ( $ft^2$ ).
- $B_{ws}$  = Water vapor in the gas stream, proportion by volume.
- $C_a$  = Acetone blank residue concentration, mg/mg.
- $C_s$  = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
- $I$  = Percent of isokinetic sampling.
- $L_1$  = Individual leakage rate observed during the leak-check conducted prior to the first component change,  $m^3/min$  ( $ft^3/min$ )
- $L_a$  = Maximum acceptable leakage rate for either a

pretest leak-check or for a leak-check following a component change; equal to 0.00057 m<sup>3</sup>/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.

- $L_i$  = Individual leakage rate observed during the leak-check conducted prior to the " $i^{th}$ " component change ( $i = 1, 2, 3 \dots n$ ), m<sup>3</sup>/min (cfm).
- $L_p$  = Leakage rate observed during the post-test leak-check, m<sup>3</sup>/min (cfm).
- $m_a$  = Mass of residue of acetone after evaporation, mg.
- $m_n$  = Total amount of particulate matter collected, mg.
- $M_w$  = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- $P_{bar}$  = Barometric pressure at the sampling site, mm Hg (in. Hg).
- $P_s$  = Absolute stack gas pressure, mm Hg (in. Hg).
- $P_{std}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- $R$  = Ideal gas constant, 0.06236  
 $[(\text{mm Hg})(\text{m}^3)]/[(\text{K})(\text{g-mole})]$   
 $\{21.85 [(\text{in. Hg})(\text{ft}^3)]/[(^\circ\text{R})(\text{lb-mole})]\}.$
- $T_m$  = Absolute average DGM temperature (see Figure

5-3), K ( $^{\circ}$ R).

$T_s$  = Absolute average stack gas temperature (see Figure 5-3), K ( $^{\circ}$ R).

$T_{std}$  = Standard absolute temperature, 293 K (528  $^{\circ}$ R).

$V_a$  = Volume of acetone blank, ml.

$V_{aw}$  = Volume of acetone used in wash, ml.

$V_{lc}$  = Total volume of liquid collected in impingers and silica gel (see Figure 5-6), ml.

$V_m$  = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$  = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$  = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

$v_s$  = Stack gas velocity, calculated by Method 2, Equation 2-7, using data obtained from Method 5, m/sec (ft/sec).

$W_a$  = Weight of residue in acetone wash, mg.

$Y$  = Dry gas meter calibration factor.

$\Delta H$  = Average pressure differential across the orifice meter (see Figure 5-4), mm H<sub>2</sub>O (in. H<sub>2</sub>O).

$D_a$  = Density of acetone, mg/ml (see label on bottle).

$D_w$  = Density of water, 0.9982 g/ml  
(0.002201 lb/ml).

$2$  = Total sampling time, min.

$2_1$  = Sampling time interval, from the beginning of  
a run until the first component change, min.

$2_i$  = Sampling time interval, between two successive  
component changes, beginning with the interval  
between the first and second changes, min.

$2_p$  = Sampling time interval, from the final ( $n^{\text{th}}$ )  
component change until the end of the sampling  
run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

12.2 Average Dry Gas Meter Temperature and Average  
Orifice Pressure Drop. See data sheet (Figure 5-3).

12.3 Dry Gas Volume. Correct the sample volume  
measured by the dry gas meter to standard conditions (20 °C,  
760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(\text{std})} = V_m Y \frac{T_{\text{std}} (P_{\text{bar}} + \frac{H}{13.6})}{T_m P_{\text{std}}}$$

$$= K_1 V_m Y \frac{P_{\text{bar}} + (\frac{H}{13.6})}{T_m}$$

**Eq. 5-1**

where:

$$K_1 = 0.3858 \text{ } ^\circ\text{K/mm Hg for metric units,}$$

$$= 17.64 \text{ } ^\circ\text{R/in. Hg for English units.}$$

**NOTE:** Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds  $L_a$ . If  $L_p$  or  $L_i$  exceeds  $L_a$ , Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace  $V_m$  in Equation 5-1 with the expression:

$$[V_m - (L_p - L_a) \mathbf{2}]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace  $V_m$  in Equation 5-1 by the expression:

$$\left[ V_m - (L_1 - L_a) \mathbf{2}_1 - \sum_{i=2}^n (L_i - L_a) \mathbf{2}_i - (L_p - L_a) \mathbf{2}_p \right]$$

and substitute only for those leakage rates ( $L_i$  or  $L_p$ ) which exceed  $L_a$ .

#### 12.4 Volume of Water Vapor Condensed.

$$V_{w(\text{std})} = V_{lc} \frac{D_w R T_{\text{std}}}{M_w P_{\text{std}}}$$

$$= K_2 V_{lc}$$

**Eq. 5-2**

where:

$$\begin{aligned} K_2 &= 0.001333 \text{ m}^3/\text{ml} \text{ for metric units,} \\ &= 0.04706 \text{ ft}^3/\text{ml} \text{ for English units.} \end{aligned}$$

#### 12.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad \text{Eq. 5-3}$$

**NOTE:** In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of  $B_{ws}$  shall be considered correct. The procedure for determining the moisture content based upon the assumption of saturated conditions is given in Section 4.0 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-3 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ).

#### 12.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a D_a} \quad \text{Eq. 5-4}$$

#### 12.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} D_a \quad \text{Eq. 5-5}$$

12.8 Total Particulate Weight. Determine the total particulate matter catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5-6).

**NOTE:** In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight. Refer to Section 8.5.8 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

## 12.9 Particulate Concentration.

$$C_s = \frac{K_3 m_h}{V_{m(std)}} \quad \text{Eq. 5-6}$$

where:

$K_3 = 0.001 \text{ g/mg}$  for metric units.

$= 0.0154 \text{ gr/mg}$  for English units.

## 12.10 Conversion Factors:

<u>From</u>	<u>To</u>	<u>Multiply by</u>
ft <sup>3</sup>	m <sup>3</sup>	0.02832
gr	mg	64.80004
gr/ft <sup>3</sup>	mg/m <sup>3</sup>	2288.4
mg	g	0.001
gr	lb	$1.429 \times 10^{-4}$

## 12.11 Isokinetic Variation.

## 12.11.1 Calculation from Raw Data.

$$I = \frac{100 T_s \left[ K_4 V_{lc} + \frac{(V_m Y)}{T_m} \left( P_{bar} + \frac{H}{13.6} \right) \right]}{60 \cdot 2 \cdot v_s \cdot P_s \cdot A_n} \quad \text{Eq. 5-7}$$

where:

$K_4 = 0.003454 [(\text{mm Hg})(\text{m}^3)]/[(\text{ml})(^\circ\text{K})]$  for metric units,

$= 0.002669 [(\text{in. Hg})(\text{ft}^3)]/[(\text{ml})(^\circ\text{R})]$  for English units.

## 12.11.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s 2 A_n P_s 60 (1 - B_{ws})}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n 2 (1 - B_{ws})} \quad \text{Eq. 5-8}$$

where:

$K_5 = 4.320$  for metric units,

$= 0.09450$  for English units.

12.11.3 Acceptable Results. If 90 percent  $\leq I \leq$  110 percent, the results are acceptable. If the PM results are low in comparison to the standard, and "I" is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in Section 17.0 may be used to make acceptability judgments. If "I" is judged to be unacceptable, reject the results, and repeat the sampling run.

12.12 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 12.3 and 12.4 of Method 2.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures.

16.1 Dry Gas Meter as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 10.3, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard Dry Gas Meter Calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity [e.g., 3 liters/rev (0.1 ft<sup>3</sup>/rev)]. A spirometer [400 liters (14 ft<sup>3</sup>) or more capacity], or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft<sup>3</sup>/rev) and capable of measuring volume to within 1.0 percent. Wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5-7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test

meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized [no greater than 100 mm H<sub>2</sub>O (4 in. H<sub>2</sub>O) at a flow rate of 30 liters/min (1 cfm)]. This can be accomplished by using large diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate,  $Q$ , for each run using the wet test meter volume,  $V_w$ , and the run time, **2**. Calculate the DGM coefficient,  $Y_{ds}$ , for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar} V_w}{(T_w + T_{std}) \mathbf{2}} \quad \text{Eq. 5-9}$$

$$Y_{ds} = \frac{V_w (T_{ds} + T_{std}) P_{bar}}{V_{ds} (T_w + T_{std}) \left( P_{bar} + \frac{)P}{13.6} \right)} \quad \text{Eq. 5-10}$$

where:

$$\begin{aligned} K_1 &= 0.3858 \text{ } ^\circ\text{C/mm Hg for metric units} \\ &= 17.64 \text{ } ^\circ\text{F/in. Hg for English units.} \end{aligned}$$

- $V_w$  = Wet test meter volume, liter ( $\text{ft}^3$ ).  
 $V_{ds}$  = Dry gas meter volume, liter ( $\text{ft}^3$ ).  
 $T_{ds}$  = Average dry gas meter temperature,  $^{\circ}\text{C}$  ( $^{\circ}\text{F}$ ).  
 $T_{adj}$  = 273  $^{\circ}\text{C}$  for metric units  
           = 460  $^{\circ}\text{F}$  for English units.  
 $T_w$  = Average wet test meter temperature,  $^{\circ}\text{C}$  ( $^{\circ}\text{F}$ ).  
 $P_{bar}$  = Barometric pressure, mm Hg (in. Hg).  
 $\Delta p$  = Dry gas meter inlet differential pressure,  
       mm  $\text{H}_2\text{O}$  (in.  $\text{H}_2\text{O}$ ).  
**2** = Run time, min.

16.1.1.5 Compare the three  $Y_{ds}$  values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three  $Y_{ds}$  values at each flow rate resulting in no less than five average meter coefficients,  $Y_{ds}$ .

16.1.1.6 Prepare a curve of meter coefficient,  $Y_{ds}$ , versus flow rate,  $Q$ , for the DGM. This curve shall be used

as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

#### 16.1.2 Standard Dry Gas Meter Recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 30 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

#### 16.2 Critical Orifices As Calibration Standards.

Critical orifices may be used as calibration standards in place of the wet test meter specified in Section 16.1,

provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of Critical Orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (*i.e.*, a critical vacuum can be obtained, as described in Section 16.2.2.2.3). Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min (0.35 and 1.2 cfm) or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 5-1 in Section 18.0 give the approximate flow rates.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 by 20 mm sleeve type, into a ½-inch Swagelok (or

equivalent) quick connect. Insert the needle into the stopper as shown in Figure 5-9.

16.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in Section 6.1.1.9 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used (*i.e.*, there should be no connections to the inlet of the orifice).

16.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then turn on the pump, and determine whether there is any leakage. The leakage rate shall be zero (*i.e.*, no detectable movement of the DGM dial shall be seen for 1 minute).

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See Section 8.4.1 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in Section 10.3. Make sure that the wet test meter meets the requirements stated in Section 16.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor,  $Y$ .

16.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5-10.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

16.2.2.2.2 Leak check the system as in Section 16.2.2.1.1. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading,  $Y_H$ . Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section 6.1.2. Record the barometric pressure,  $P_{\text{bar}}$ , in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve  $\pm 0.5$  percent in  $K'$  (see Eq. 5-11). Record the information listed in Figure 5-11.

16.2.2.2.6 Calculate  $K'$  using Equation 5-11.

$$K' = \frac{K_1 V_m Y (P_{\text{bar}} + \frac{H}{13.6}) T_{\text{amb}}^{1/2}}{P_{\text{bar}} T_m^2} \quad \text{Eq. 5-11}$$

where:

$K'$  = Critical orifice coefficient,  $[\text{m}^3)(^\circ\text{K})^{1/2}] / [(\text{mm Hg})(\text{min})] \{ [(\text{ft}^3)(^\circ\text{R})^{1/2}] / [(\text{in. Hg})(\text{min})] \}$ .

$T_{\text{amb}}$  = Absolute ambient temperature,  $^\circ\text{K}$  ( $^\circ\text{R}$ ).

Calculate the arithmetic mean of the  $K'$  values. The individual  $K'$  values should not differ by more than  $\pm 0.5$  percent from the mean value.

16.2.3 Using the Critical Orifices as Calibration Standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in Section 16.2.2. Record the information listed in Figure 5-12.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = \frac{K_1 V_m \left[ P_{bar} + \left( \frac{H}{13.6} \right) \right]}{T_m} \quad \text{Eq. 5-12}$$

$$V_{cr(std)} = K_1 \frac{P_{bar}}{\sqrt{T_{amb}}} \quad \text{Eq. 5-13}$$

$$Y = \frac{V_{cr(std)}}{V_{m(std)}} \quad \text{Eq. 5-14}$$

where:

$V_{cr(std)}$  = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

$K_1$  = 0.3858 K/mm Hg for metric units  
 = 17.64 °R/in. Hg for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than  $\pm 2$  percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to Section 16.2.2.

#### *17.0 References.*

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. December 6, 1967.
2. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0581. April 1971.
3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March 1972.
4. Smith, W.S., R.T. Shigehara, and W.F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, MO. June 14-19, 1970.

5. Smith, W.S., et al. Stack Gas Sampling Improved and Simplified With New Equipment. APCA Paper No. 67-119. 1967.
6. Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. 1967.
7. Shigehara, R.T. Adjustment in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News 2:4-11. October 1974.
8. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976 (unpublished paper).
9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 617-622.
10. Felix, L.G., G.I. Clinard, G.E. Lacy, and J.D. McCain. Inertial Cascade Impactor Substrate Media for Flue Gas Sampling. U.S. Environmental Protection Agency. Research Triangle Park, NC 27711. Publication No. EPA-600/7-77-060. June 1977. 83 pp.
11. Westlin, P.R. and R.T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration

Standards. Source Evaluation Society Newsletter. 3(1):17-30. February 1978.

12. Lodge, J.P., Jr., J.B. Pate, B.E. Ammons, and G.A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pollution Control Association. 16:197-200. 1966.

18.0 *Tables, Diagrams, Flowcharts, and Validation Data.*

**TABLE 5-1. FLOW RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS.**

Gauge/cm	Flow rate liters/min.	Gauge/cm	Flow rate liters/min.
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

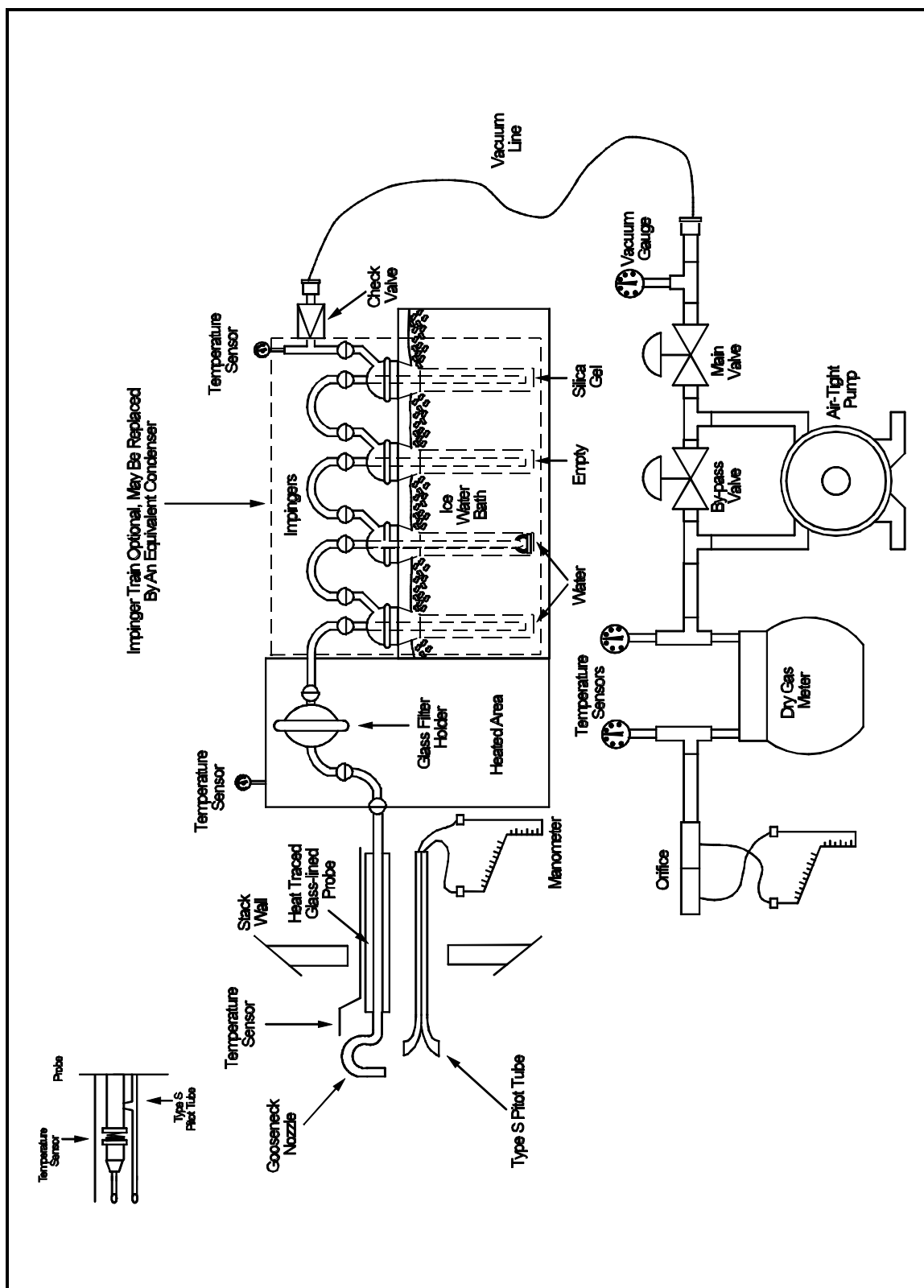


Figure 5-1. Particulate Sampling Train.

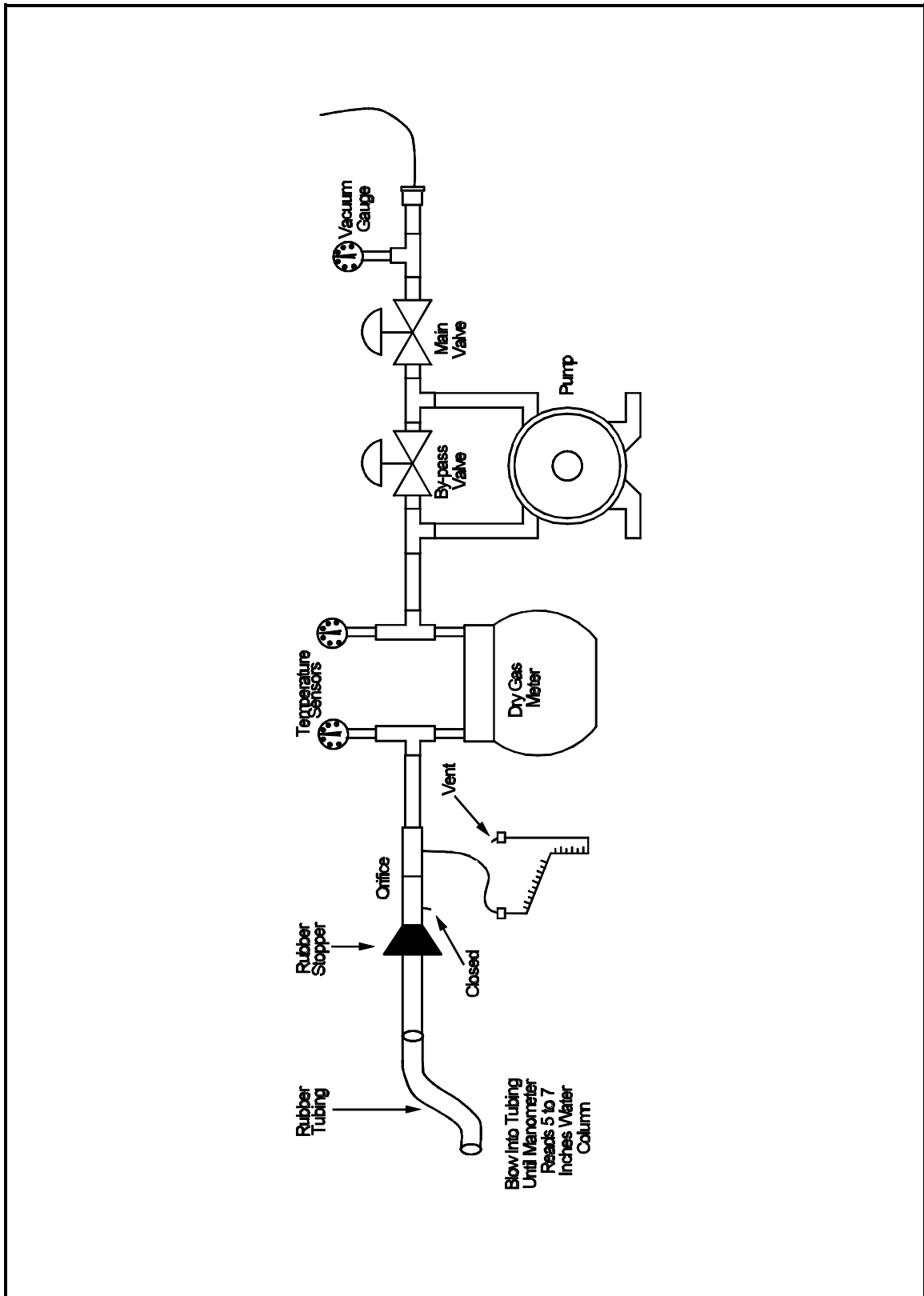


Figure 5-2. Leak Check of Meter Box.

**Figure 5-3. Particulate Field Data.**

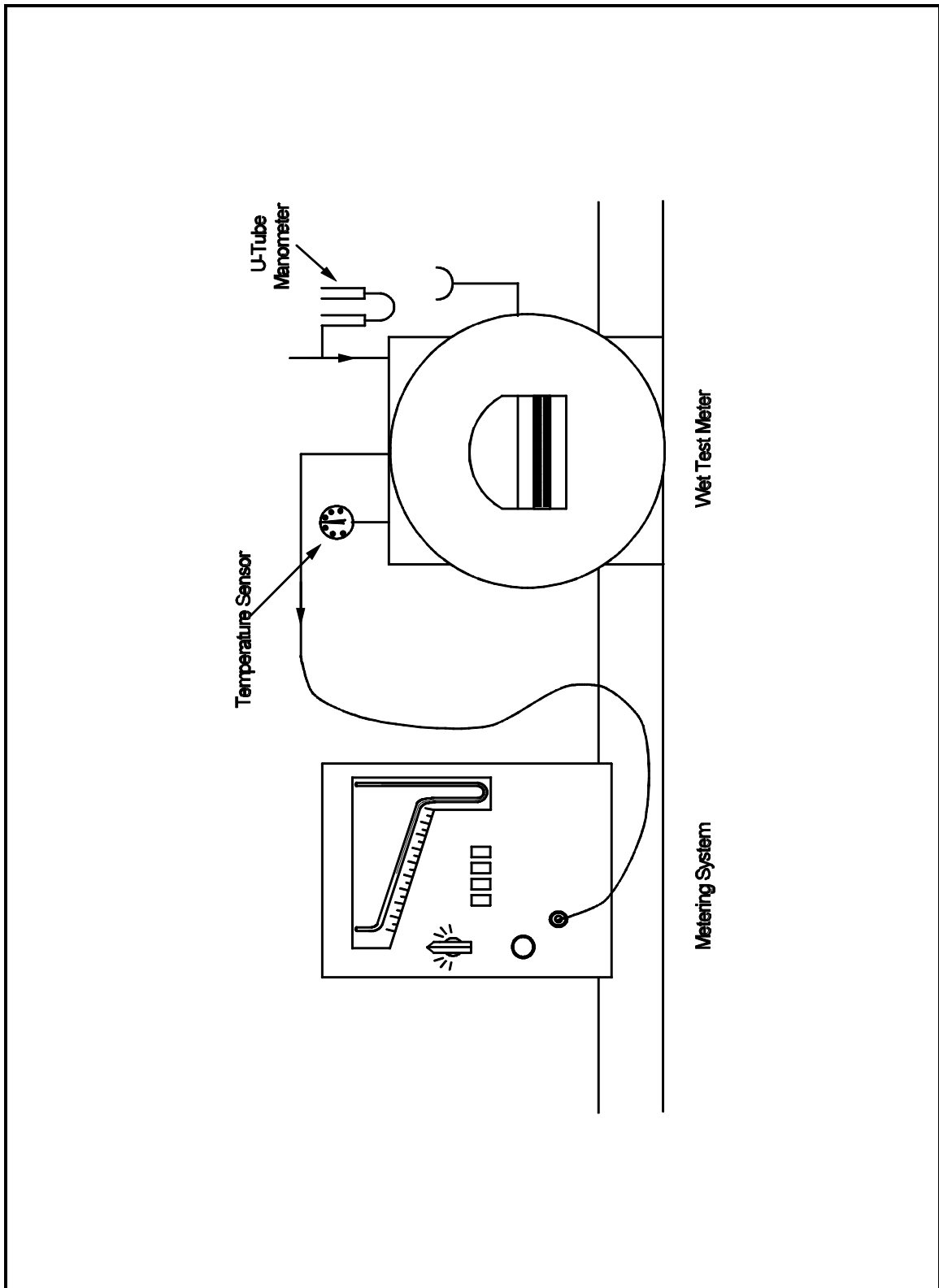


Figure 5-4. Equipment arrangement for metering system calibration.

Figure 5-5. Example Data Sheet for Calibration of Metering System (English Units).

Plant \_\_\_\_\_  
 Date \_\_\_\_\_  
 Run No. \_\_\_\_\_  
 Filter No. \_\_\_\_\_  
 Amount liquid lost during transport \_\_\_\_\_  
 Acetone blank volume, ml \_\_\_\_\_  
 Acetone blank concentration, mg/mg (Equation 5-4) \_\_\_\_\_  
 Acetone wash blank, mg (Equation 5-5) \_\_\_\_\_

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1.			
2.			
Total			
Less acetone blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final.....		
Initial.....		
Liquid collected		
Total volume collected....		g*                  ml

\*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\text{g/ml})} = \text{Volume water, ml}$$

Figure 5-6. Analytical Data Sheet.

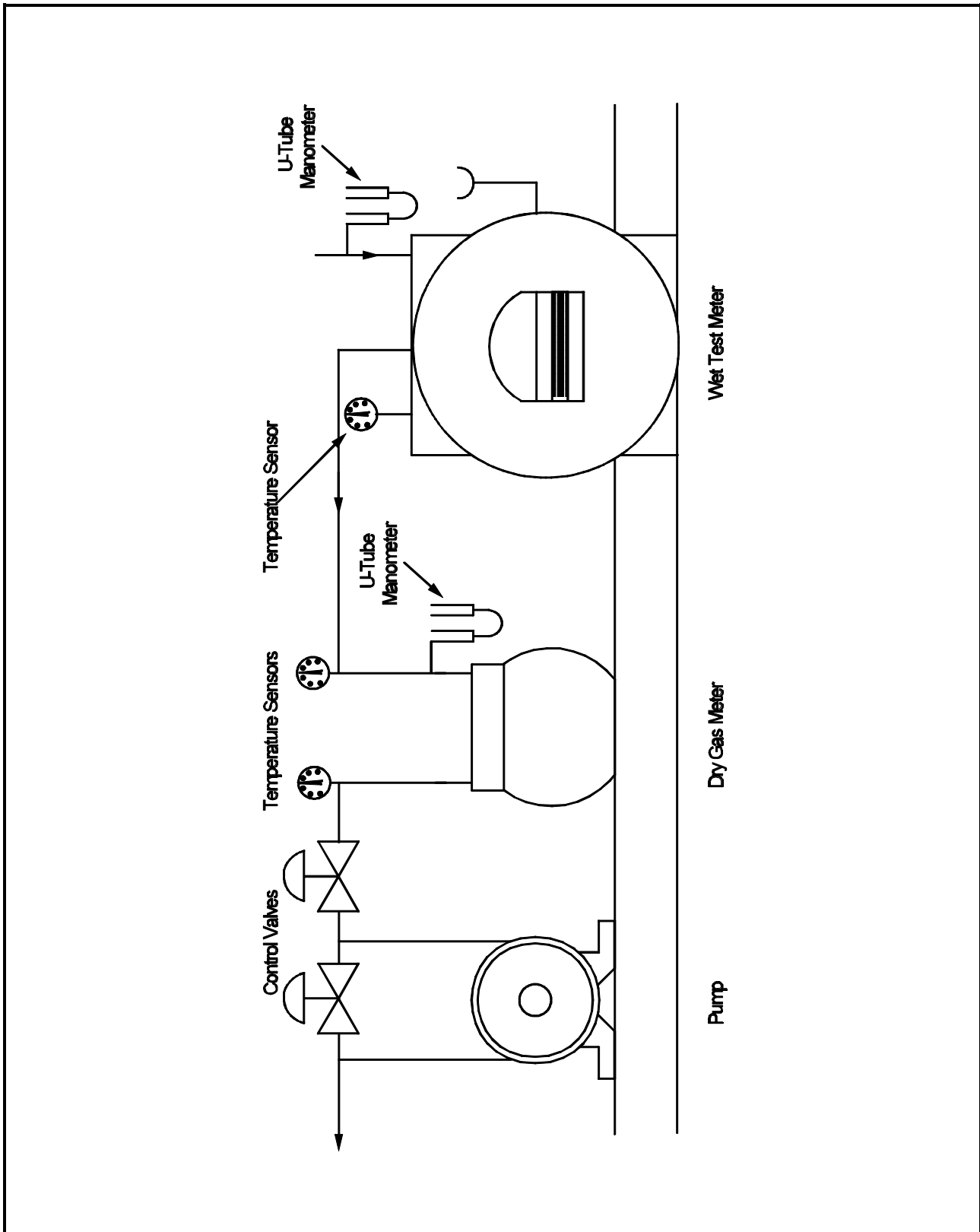


Figure 5-7. Equipment Arrangement for Dry Gas Meter Calibration.

Date: \_\_\_\_\_  
 Dry Gas Meter Identification: \_\_\_\_\_  
 Barometric Pressure (P): \_\_\_\_\_ in. Hg

Approximate Flow Rate (Q) cfm	Spirometer (Wet Meter) Gas Volume (V) ft <sup>3</sup>	Dry Gas Meter Volume (V) ft <sup>3</sup>	Temperatures			Dry Gas Meter Pressure (Δp) in. H <sub>2</sub> O	Time (t) hr	Flow Rate (Q) cfm	Meter Coefficient (V <sub>ds</sub> )	Average Meter Coefficient (V <sub>ds</sub> )
			Spirometer (Wet Meter) (t) °F	Inlet (t) °F	Outlet (t) °F					
0.40										
0.60										
0.80										
1.00										
1.20										

$$Q = K_1 \frac{P}{(T + T_w)} \frac{V_w}{(T + T_w)} \frac{Q_w}{std}$$

$$Y_{ds} = \frac{V_{ws} \frac{(T + T_w)}{std} \frac{P}{std} \frac{bar}{bar}}{V_{ds} \frac{(T + T_w)}{std} \frac{(P + P)}{std} \frac{bar}{bar} \frac{\Delta}{13.6}}$$

Figure 5-8. Example Data Sheet for Calibration of a Standard Dry Gas Meter for Method 5 Sampling Equipment (English units).

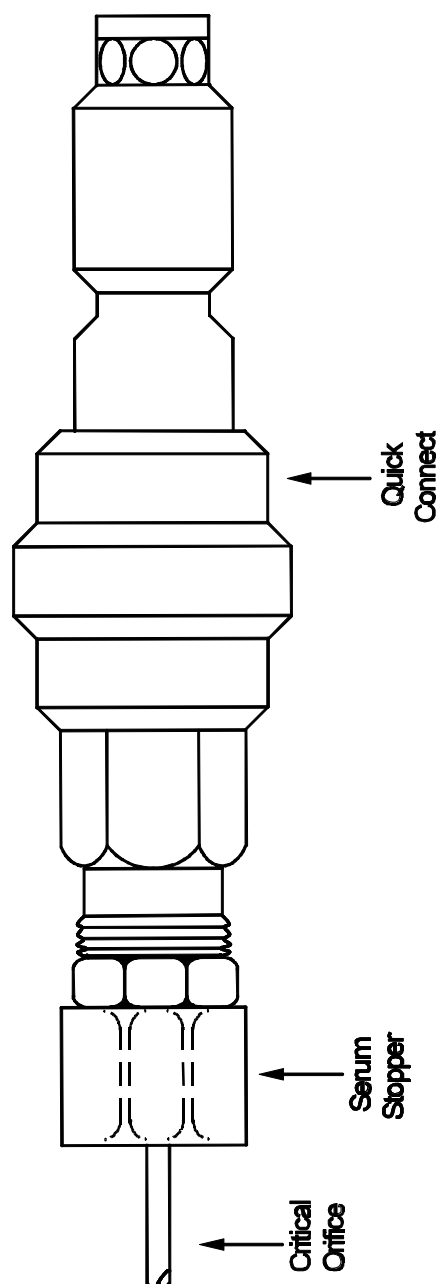


Figure 5-9. Critical Orifice Adaptation to Method 5 Metering System.

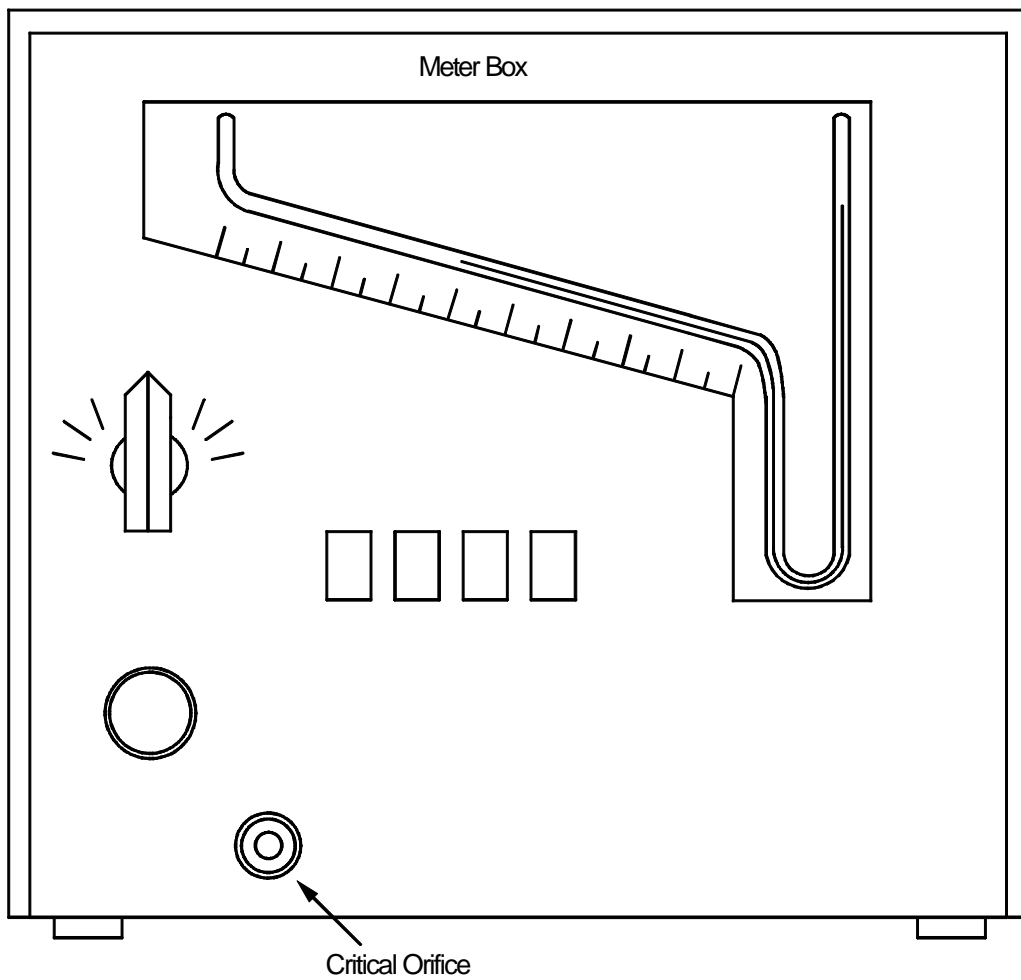


Figure 5-10. Apparatus Setup.

Date \_\_\_\_\_  
 Train ID \_\_\_\_\_  
 DGM cal. factor \_\_\_\_\_  
 Critical orifice ID \_\_\_\_\_

Dry gas meter		Run number	
		1	2
Final reading.....	m <sup>3</sup> (ft <sup>3</sup> ).....	.....	.....
Initial reading.....	m <sup>3</sup> (ft <sup>3</sup> ).....	.....	.....
Difference, V <sub>m</sub> .....	m <sup>3</sup> (ft <sup>3</sup> ).....	.....	.....
Inlet/Outlet			
temperatures:	°C (°F).....	/	/
Initial.....	°C (°F).....	/	/
.	°C (°F).....	.....	.....
Final.....	min/sec.....	/	/
.	min.....	.....	.....
Avg. Temperature,			
t <sub>m</sub>			
Time, .....			
Orifice man. rdg., ΔH..	mm (in.) H <sub>2</sub> O..	.....	.....
Bar. pressure, P <sub>bar</sub> ....	mm (in.) Hg...	.....	.....
Ambient temperature,	°C (°F).....	.....	.....
t <sub>amb</sub>	mm(in.) Hg...		
Pump vacuum.....	.....	.....	.....
K' factor.....	.....	.....	.....
Average.....		.....	.....
.			

Figure 5-11. Data sheet for determining K' factor.

Date \_\_\_\_\_  
 Train ID \_\_\_\_\_  
 Critical orifice ID \_\_\_\_\_  
 Critical orifice K' factor \_\_\_\_\_

Dry gas meter		Run number	
		1	2
Final reading . . . . .	m <sup>3</sup> (ft <sup>3</sup> ) . . . . .	.....	.....
Initial reading . . . . .	m <sup>3</sup> (ft <sup>3</sup> ) . . . . .	.....	.....
Difference, V <sub>m</sub> . . . . .	m <sup>3</sup> (ft <sup>3</sup> ) . . . . .	.....	.....
Inlet/outlet temperatures:	°C (°F) . . . . .	/	/
Initial . . . . .	°C (°F) . . . . .	/	/
Final . . . . .	°C (°F) . . . . .	.....	.....
Avg. Temperature, t <sub>m</sub> . .	min/sec . . . . .	/	/
Time, . . . . .	min . . . . .	.....	.....
Orifice man. rdg., ΔH . . .	min . . . . .	.....	.....
Bar. pressure, P <sub>bar</sub> . . . .	mm (in.) H <sub>2</sub> O . . . .	.....	.....
Ambient temperature, t <sub>amb</sub>	mm (in.) Hg . . . .	.....	.....
Pump vacuum . . . . .	°C (°F) . . . . .	.....	.....
V <sub>m(std)</sub> . . . . .	mm (in.) Hg . . . .	.....	.....
V <sub>cr(std)</sub> . . . . .	m <sup>3</sup> (ft <sup>3</sup> ) . . . . .	.....	.....
DGM cal. factor, Y . . . .	m <sup>3</sup> (ft <sup>3</sup> ) . . . . .	.....	.....
	. . . . .	.....	.....

Figure 5-12. Data sheet for determining DGM Y Factor.

## **Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors**

### **1. APPLICABILITY AND PRINCIPLE**

**1.1 Applicability.** This method is applicable to the determination of emissions of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

**1.2 Principle.** A sample is withdrawn isokinetically from the gas stream and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle and vapor fraction. The PCDD's and PCDF's are extracted from the sample, separated by high resolution gas chromatography (HRGC), and measured by high resolution mass spectrometry (HRMS).

### **2. APPARATUS**

**2.1 Sampling.** A schematic of the sampling train is shown in Figure 23-1. Sealing greases **may** not be used in assembling the train. The train is identical to that described in Section 2.1 of Method 5 of this appendix with the following additions:

**2.1.1 Nozzle.** The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

**2.1.2 Sample Transfer Lines.** The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with 1/8 in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120°C.

**2.1.1 Filter Support.** Teflon or Teflon-coated wire.

**2.1.2 Condenser.** Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

**2.1.3 Water Bath.** Thermostatically controlled to maintain the gas temperature exiting the condenser at 20°C (68°F).

**2.1.4 Adsorbent Module.** Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 23-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

## **2.2 Sample Recovery.**

**2.2.1 Fitting Caps.** Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train and sorbent module.

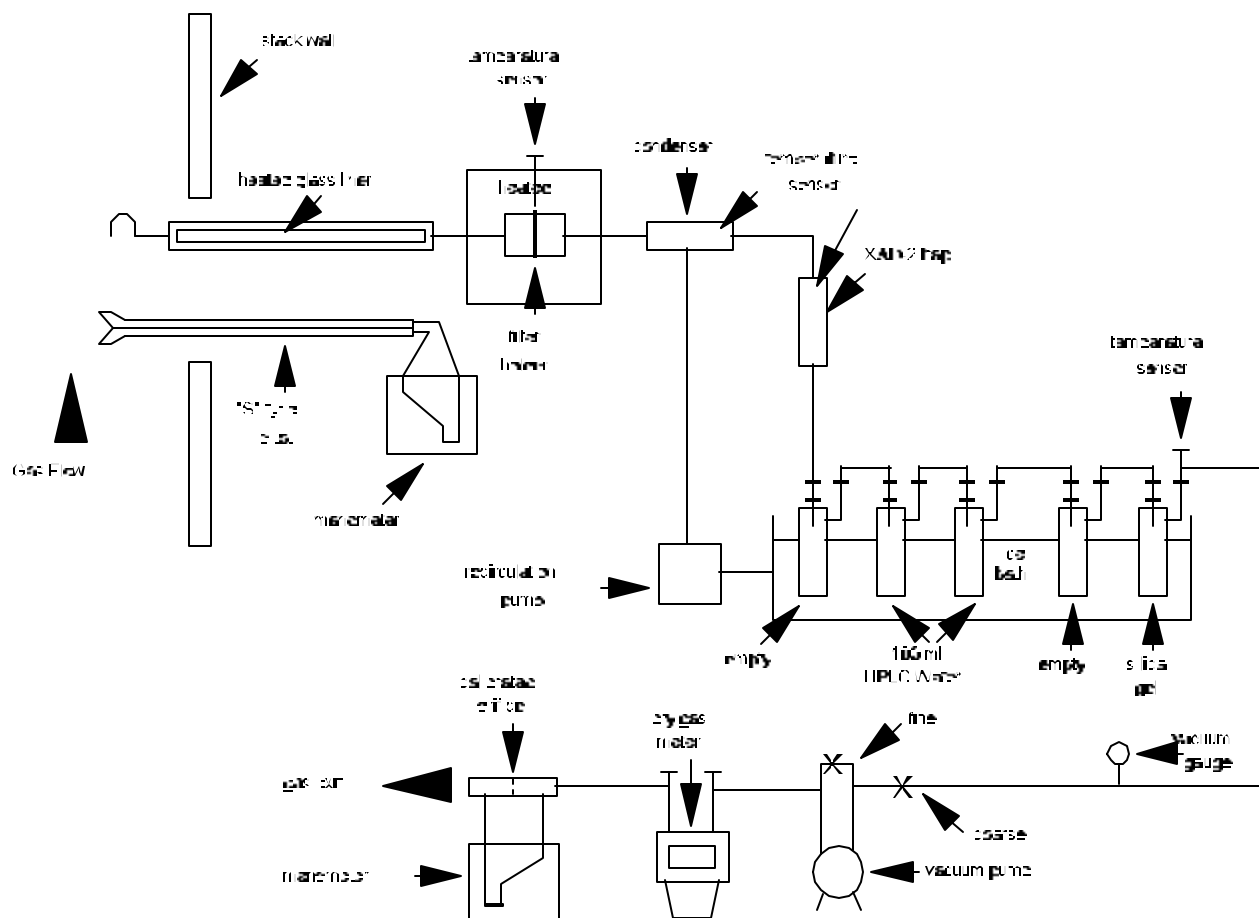
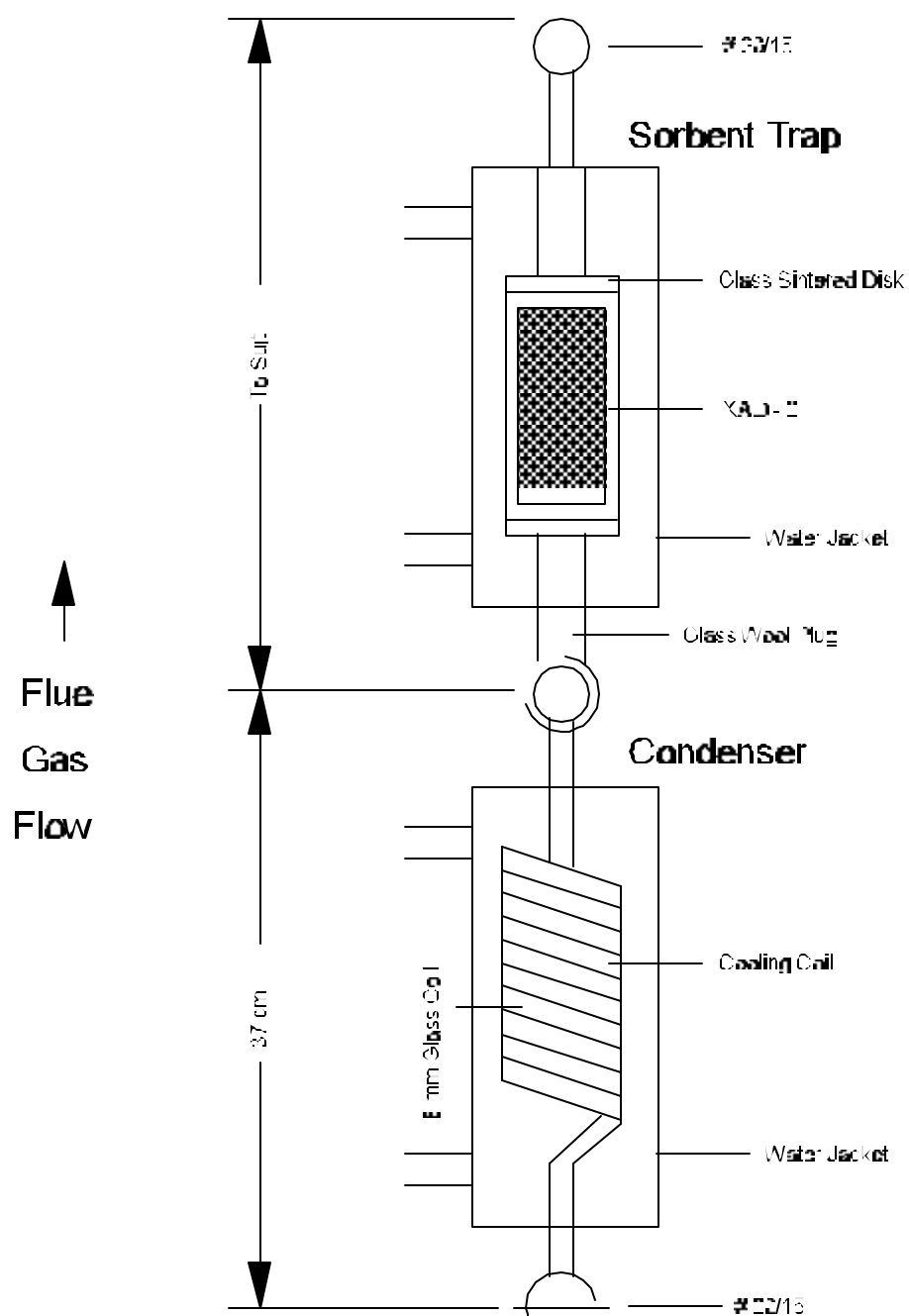


Figure 23.1 Sampling Train



**Figure 23.2 Condenser and Adsorbent Trap**

**2.2.2 Wash Bottles.** Teflon, 500-mL.

**2.2.3 Probe Liner, Probe Nozzle, and Filter Holder Brushes.** Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

**2.2.4 Filter Storage Container.** Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, glass petri dish.

**2.2.5 Balance.** Triple beam.

**2.2.6 Aluminum Foil.** Heavy duty, hexane-rinsed.

**2.2.7 Metal Storage Container.** Air tight container to store silica gel.

**2.2.8 Graduated Cylinder.** Glass, 250-mL with 2-mL graduations.

**2.2.9 Glass Sample Storage Containers.** Amber glass bottles for sample glassware washes, 500- or 1000-mL, with leak free Teflon-lined caps.

## **2.3 Analysis.**

**2.3.1 Sample Containers.** 125- and 250-mL flint glass bottles with Teflon-lined caps.

**2.3.2 Test Tubes.** Glass.

**2.3.3 Soxhlet Extraction Apparatus.** Capable of holding 43 x 123 mm extraction thimbles.

**2.3.4 Extraction Thimble.** Glass, precleaned cellulosic, or glass fiber.

**2.3.5 Pasteur Pipettes.** For preparing liquid chromatographic columns.

**2.3.6 Reacti-vials.** Amber glass, 2-mL, silanized prior to use.

**2.3.7 Rotary Evaporator.** Buchi/Brinkman RF-121 or equivalent.

**2.3.8 Nitrogen Evaporative Concentrator.** N-Evap Analytical Evaporator Model III or equivalent.

**2.3.9 Separatory Funnels.** Glass, 2-liter.

**2.3.10 Gas Chromatograph.** Consisting of the following components:

**2.3.10.1 Oven.** Capable of maintaining the separation column at the proper operating temperature  $\pm 10^{\circ}\text{C}$  and performing programmed increases in temperature at rates of at least  $40^{\circ}\text{C}/\text{min}$ .

**2.3.10.2 Temperature Gauges.** To monitor column oven, detector, and exhaust temperatures  $\pm 1^{\circ}\text{C}$ .

**2.3.10.3 Flow Systems.** Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

**2.3.10.4 Capillary Columns.** A fused silica column, 60 x 0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m x 0.25 mm ID coated with DB-225. Other column systems may be substituted provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of Section 6.1.2.2.

**2.3.11 Mass Spectrometer.** Capable of routine operation at a resolution of 1:10000 with a stability of  $\pm 5$  ppm.

**2.3.12 Data System.** Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

**2.3.13 Analytical Balance.** To measure within 0.1 mg.

### 3. REAGENTS

#### 3.1 Sampling.

**3.1.1 Filters.** Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency ( $<0.05$  percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference - see §60.17).

**3.1.1.1 Precleaning.** All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean nitrogen ( $\text{N}_2$ ) stream. Store the filters in a glass petri dish sealed with Teflon tape.

**3.1.2 Adsorbent Resin.** Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

**3.1.2.1 Cleaning.** Procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

<u>Solvent</u>	<u>Procedure</u>
Water	Initial Rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

### **3.1.2.2 Drying.**

**3.1.2.2.1 Drying Column.** Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

**3.1.2.2.2 Procedure.** The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source for large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles, but not so excessive as to cause the particles to fracture.

**3.1.2.3 Quality Control Check.** The adsorbent must be checked for residual toluene prior to use.

**3.1.2.3.1 Extraction.** Weigh a 1.0 g sample of dried resin into a small vial, add 3 mL of toluene, cap the vial, and shake it well.

**3.1.2.3.2 Analysis.** Inject a 2 : 1 sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x 1/8 in stainless steel containing 10 percent OV-101™ on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 mL/min.

Detector: Flame ionization detector operated at a sensitivity of  $4 \times 10^{-11}$  A/mV.

Injection Port Temperature: 250°C.

Detector Temperature: 305°C.

Oven Temperature: 30°C for 4 min; programmed to rise at 40°C/min until it reaches 250°C; return to 30°C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 2.5 : l of methylene chloride into 100 mL of toluene. This corresponds to 100 : g of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 : g/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

**3.1.2.4 Storage.** The adsorbent must be used within 4 weeks of cleaning. After cleaning, the adsorbent may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

**3.1.3 Glass Wool.** Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110°C oven, and stored in a methylene chloride-washed glass container with a Teflon-lined screw cap.

**3.1.4 Water.** Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

**3.1.5 Silica Gel.** Indicating type, 6 to 16 mesh. If previously used, dry at 175° C (350°F) for two hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

**3.1.6 Chromic Acid Cleaning Solution.** Dissolve 20 g of sodium dichromate in 15 mL of water, and then carefully add 400 mL of concentrated sulfuric acid.

## **3.2 Sample Recovery.**

**3.2.1 Acetone.** Pesticide quality.

**3.2.2 Methylene Chloride.** Pesticide quality.

**3.2.3 Toluene.** Pesticide quality.

## **3.3 Analysis.**

**3.3.1 Potassium Hydroxide.** ACS grade, 2-percent (weight/volume) in water.

**3.3.2 Sodium Sulfate.** Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

**3.3.3 Sulfuric Acid.** Reagent grade.

**3.3.4 Sodium Hydroxide.** 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

**3.3.5 Hexane.** Pesticide grade.

**3.3.6 Methylene Chloride.** Pesticide grade.

**3.3.7 Benzene.** Pesticide grade.

**3.3.8 Ethyl Acetate.**

**3.3.9 Methanol.** Pesticide grade.

**3.3.10 Toluene.** Pesticide grade.

**3.3.11 Nonane.** Pesticide grade.

**3.3.12 Cyclohexane.** Pesticide Grade.

**3.3.13 Basic Alumina.** Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130°C. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

**3.3.14 Silica Gel.** Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180°C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50°C for 10 minutes, then increase the temperature gradually to 180°C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

**3.3.15 Silica Gel Impregnated with Sulfuric Acid.** Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

**3.3.16 Silica Gel Impregnated with Sodium Hydroxide.** Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

**3.3.17 Carbon/Celite.** Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-mL glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

**3.3.18 Nitrogen.** Ultra high purity.

**3.3.19 Hydrogen.** Ultra high purity.

**3.3.20 Internal Standard Solution.** Prepare a stock standard solution containing the isotopically labeled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 mL of nonane.

**3.3.21 Surrogate Standard Solution.** Prepare a stock standard solution containing the isotopically labeled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 mL of nonane.

**3.3.22 Recovery Standard Solution.** Prepare a stock standard solution containing the isotopically labeled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 mL of nonane.

## **4. PROCEDURE**

**4.1 Sampling.** The complexity of this method is such that, in order to obtain reliable results, testers and analysts should be trained and experienced with the procedures.

### **4.1.1 Pretest Preparation.**

**4.1.1.1 Cleaning Glassware.** All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

**4.1.1.2 Adsorbent Trap.** The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 : 1 of the surrogate standard solution (Section 3.3.21) to each trap.

**4.1.1.3 Sampling Train.** It is suggested that all components be maintained according to the procedure described in APTD-0576.

**4.1.1.4 Silica Gel.** Weigh several 200 to 300 g portions of silica gel in air tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an

alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

**4.1.1.5 Filter.** Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

**4.1.2 Preliminary Determinations.** Same as Section 4.1.2 of Method 5.

**4.1.3 Preparation of Collection Train.**

**4.1.3.1** During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until sampling is about to begin.

**4.1.3.2** Place approximately 100 mL of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

**4.1.3.3** Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus the fifth impinger may be determined to the nearest 0.5 g and recorded.

**4.1.3.4** Assemble the sampling train as shown in Figure 23-1.

**4.1.3.5** Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50°C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C for efficient capture of the PCDD's and PCDF's.

**4.1.4 Leak-Check Procedure.** Same as Method 5, Section 4.1.4.

**4.1.5 Sampling Train Operation.** Same as Method 5, Section 4.1.5.

**4.2 Sample Recovery.** Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

**4.2.1 Container No. 1.** Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Do not place the filter in aluminum foil. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

**4.2.2 Adsorbent Module.** Remove the module from the train, tightly cap both ends, label it, and store it on ice for transport to the laboratory.

**4.2.3 Container No. 2.** Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

**4.2.4 Container No. 3.** Repeat the methylene chloride-rinsing described in Section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

**4.2.5 Impinger Water.** Measure the liquid in the first four impingers to within 1 mL by using a graduated cylinder or by weighing it to within 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight.

**4.2.7 Silica Gel.** Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

## **5. ANALYSIS**

All glassware shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

### **5.1 Sample Extraction.**

**5.1.1 Extraction System.** Place an extraction thimble (Section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

**5.1.2 Container No. 1 (Filter).** Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

**5.1.3 Adsorbent Cartridge.** Suspend the adsorbent module directly over the extraction thimble in the beaker (See Section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug to the thimble.

**5.1.4 Container No. 2 (Acetone and Methylene Chloride).** Concentrate the sample to a volume of about 1-2 mL using the rotary evaporator apparatus at a temperature of less than 37°C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the sampling train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in Section 5.1.1.

**5.1.5 Extraction.** Add 100 : 1 of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from Section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-mL rinses to the rotary evaporator. Concentrate the extract to approximately 10 mL. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other half according to the procedures in Sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 mL of hexane.

**5.1.6 Container No. 3 (Toluene Rinse).** Add 100 : 1 of the internal standard solution (Section 3.3.20) to the contents of the container. Concentrate the sample to a volume of about 1-5 mL using the rotary evaporator apparatus at a temperature of less than 37°C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in Sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

## **5.2 Sample Cleanup and Fractionation.**

**5.2.1 Silica Gel Column.** Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 mL of hexane and discard. Add the sample extract, dissolved in 5 mL of hexane to the column with two additional 5-mL rinses. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 mL using the nitrogen evaporative concentrator (Section 2.3.8).

**5.2.2 Basic Alumina Column.** Shorten a 25-mL disposable Pasteur pipette to about 16 mL. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 mL of 0.5 percent methylene chloride in hexane followed by 120 mL of 35 percent methylene chloride in hexane. Discard the first 120 mL of eluate. Collect the second 120 mL of eluate and concentrate it to about 0.5 mL using the nitrogen evaporative concentrator.

**5.2.3 AX-21 Carbon/Celite 545 Column.** Remove the bottom 0.5 in. from the tip of a 9-mL disposable Pasteur pipette. Insert a glass fiber filter disk or glass wool plug in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/Celite™ mixture to form a 2 cm column (the 0.6 mL mark column). Top with a glass wool plug. In some cases AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 mL of 50 percent benzene in ethyl acetate, 1 mL of a 50 percent methylene chloride in cyclohexane mixture, and 2 mL of hexane. Discard these rinses. Transfer the concentrate in 1 mL hexane from the basic alumina column to the carbon/celite along with 1 mL of hexane rinse. Elute the column sequentially with 2 mL of 50 percent methylene chloride in hexane and 2 mL of 50 percent benzene in ethyl acetate and discard the eluates. Invert the column and elute in the reverse direction with 13 mL of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50°C to about 1 mL. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N<sub>2</sub>. Store extracts at room temperature, shielded from light, until the analysis is performed.

**5.3 Analysis.** Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in Sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 : 1 aliquot of the recovery standard solution from Table 1 to each sample. A 2 : 1 aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of Section 6.1.2.2.

### **5.3.1 Gas Chromatograph Operating Conditions.**

**5.3.1.1 Injector.** Configured for capillary column, splitless, 250 °C.

**5.3.1.2 Carrier Gas.** Helium, 1-2 ml/min.

**5.3.1.3 Oven.** Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then by °C/min up to 300 °C.

**5.3.2 High Resolution Mass Spectrometer.**

**5.3.2.1 Resolution.** 10,000 m/e.

**5.3.2.2 Ionization Mode.** Electron impact.

**5.3.2.3 Source Temperature 250°C.**

**5.3.2.4 Monitoring Mode.** Selected ion monitoring. A list of the various ions to be monitored is presented in Table 3.

**5.3.2.5 Identification Criteria.** The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio ( $M/M+2$  or  $M+2/M+4$ ) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges ( $\pm 15\%$ ) for the identification of chlorine-containing compounds are given in Table 4.
2. The retention time for the analytes must be within 3 seconds of the corresponding  $^{13}\text{C}$ -labeled internal standard or surrogate standard.
3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.
4. The identification of specific isomers that do not have corresponding  $^{13}\text{C}$ -labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.
5. The signal to noise ratio for all monitored ions must be greater than 2.5.
6. The confirmation of 2, 3, 7, 8-TCDF shall satisfy all of the above identification criteria.
7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

**5.3.2.6 Quantification.** The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the  $^{13}\text{C}_{12}$ -2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-

HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

## 6. CALIBRATION

Same as Method 5 with the following additions.

### 6.1 GC/MS System.

**6.1.1 Initial Calibration.** Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal and surrogate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

#### 6.1.2 Daily Performance Check.

**6.1.2.1 Calibration Check.** Inject one : 1 of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

**6.1.2.2 Column Separation Check.** Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

**6.2 Lock Channels.** Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

## 7. QUALITY CONTROL

**7.1 Sampling Train Collection Efficiency Check.** Add 100 : 1 of the surrogate standards in Table 1 to the adsorbent cartridge of each train before collecting the field samples.

**7.2 Internal Standard Percent Recoveries.** A group of nine carbon-labeled PCDDs and PCDFs representing the tetra- through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in

the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra- through hexachlorinated compounds while the range is 25 to 130 percent for the hepta- and octachlorinated homologues.

**7.3 Surrogate Standard Recoveries.** The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of the collection efficiency. They are not used to measure the native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

**7.4 Toluene QA Rinse.** Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

## **8. QUALITY ASSURANCE**

**8.1 Applicability.** When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

**8.2 Audit Procedure.** Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

**8.3 Audit Sample Availability.** Audit samples will be supplied only to enforcement agencies for compliance tests. Audit samples may be obtained by writing:

Source Test Audit Coordinator (MD-77B)  
Quality Assurance Division  
Atmospheric Research and Exposure Assessment Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The audit sample request must be made at least 30 days prior to the scheduled compliance sample analysis.

**8.4 Audit Results.** Calculate the audit sample concentration according to the calculation procedure provided in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions.

Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 9. CALCULATIONS

Same as Method 5, Section 6 with the following additions.

### 9.1 Nomenclature.

$A_{ai}$	=	Integrated ion current of the noise at the retention time of the analyte.
$A_{ci}^*$	=	Integrated ion current of the two ions characteristic of the internal standard $i$ in the calibration standard.
$A_{cij}$	=	Integrated ion current of the two ions characteristic of compound $i$ in the $j$ th calibration standard.
$A_{cij}^*$	=	Integrated ion current of the two ions characteristic of the internal standard $i$ in the $j$ th calibration standard.
$A_{csi}$	=	Integrated ion current of the two ions characteristic of surrogate compound $i$ in the calibration standard.
$A_i$	=	Integrated ion current of the two ions characteristic of compound $i$ in the sample.
$A_i^*$	=	Integrated ion current of the two ions characteristic of internal standard $i$ in the sample.
$A_{rs}$	=	Integrated ion current of the two ions characteristic of the recovery standard.
$A_{si}$	=	Integrated ion current of the two ions characteristic of surrogate compound $i$ in the sample.
$C_i$	=	Concentration of PCDD or PCDF $i$ in the sample, pg/M <sup>3</sup> .
$C_T$	=	Total concentration of PCDD's or PCDF's in the sample, pg/M <sup>3</sup> .
$m_{ci}$	=	Mass of compound $i$ in the calibration standard injected into the analyzer, pg.
$m_{ci}^*$	=	Mass of labeled compound $i$ in the calibration standard injected into the analyzer, pg.
$m_i^*$	=	Mass of internal standard $i$ added to the sample, pg.
$m_{rs}$	=	Mass of recovery standard in the calibration standard injected into the analyzer, pg.
$m_s$	=	Mass of surrogate compound in the sample to be analyzed, pg.
$m_{si}$	=	Mass of surrogate compound $i$ in the calibration standard, pg.
$RRF_i$	=	Relative response factor for compound $i$ .
$RRF_{rs}$	=	Recovery standard response factor.
$RRF_s$	=	Surrogate compound response factor.
$V_{m(std)}$	=	Metered volume of sample run, dscm.

### 9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n} \frac{\sum_{j=1}^n \frac{A_{oif} m_{oi}^*}{A_{oif} m_{oi}^*}}{\quad} \quad \text{Eq. 23- 1}$$

### 9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{std}} \quad \text{Eq. 23- 2}$$

### 9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{oi}^* m_{rs}}{A_{rs} m_{oi}^*} \quad \text{Eq. 23- 3}$$

### 9.5 Recovery of Internal Standards (R<sup>\*</sup>).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \quad \text{Eq. 23- 4}$$

### 9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{oi}^* m_{si}}{A_{osi} m_{oi}^*} \quad \text{Eq. 23- 5}$$

### 9.7 Recovery of Surrogate Compounds (R<sub>s</sub>).

$$R_s = \frac{A_{si} m_i^*}{A_i^* RRF_s m_s} \times 100\% \quad \text{Eq. 23-6}$$

### 9.8 Minimum Detectable Limit (DL).

$$MDL = \frac{2.5 A_{si} m_i^*}{A_i^* RRF_i} \quad \text{Eq. 23-7}$$

### 9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_T = \sum_{i=1}^n C_i \quad \text{Eq. 23-11}$$

Any PCDDs or PCDFs that are reported as nondetected (below the DL) shall be counted as zero for the purpose of calculating the total concentration of PCDDs and PCDFs in the sample.

## 10. BIBLIOGRAPHY

1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington DC. December 1984. 25 p.
2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.
3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.
4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.
5. U.S. Environmental Protection Agency. Method 8290 - The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas

Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW-846.

Analyte	Concentration (pg/: l)
S)))))))))))))	Q)))))))))))))

<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	100	
<sup>13</sup> C <sub>12</sub> -OCDD	100	
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF		100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	100	

<sup>37</sup> Cl <sub>4</sub> -2,3,7,8-TCDD	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	100
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	100

<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	100

[illegible]

[illegible]

### Unlabeled Analytes

### Internal Standards

<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -OCDD	200	200	200	200	200
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	100	100	100	100	100

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))) Q  
(Continued)

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## Surrogate Standards

## Recovery Standards

[illegible]



**W**

Descriptor number	Accurate mass	Ion type	Elemental composition	Analyte
3	373.8208	M+2	C <sub>12</sub> H <sub>2</sub> 35Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF
	375.8178	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDF
	383.8639	M	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> O	HxCDF (S)
	385.8610	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF (S)
	389.8157	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD
	391.8127	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HxCDD
	392.9760	LOCK	C <sub>9</sub> F <sub>15</sub>	PFK
	401.8559	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD (S)
	403.8529	M+4	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDD (S)
	445.7555	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDPE
	430.9729	QC	C <sub>9</sub> F <sub>17</sub>	PFK

TABLE 23-3. (Continued)

Descriptor number	Accurate mass	Ion type	Elemental composition	Analyte
4	407.7818	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF
	409.7789	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O	HpCDF
	417.8253	M	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> O	HpCDF (S)
	389.8157	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD
	391.8127	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HxCDD
	392.9760	LOCK	C <sub>9</sub> F <sub>15</sub>	PFK
	401.8559	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD (S)
	403.8529	M+4	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDD (S)
	445.7555	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDPE
	430.9729	QC	C <sub>9</sub> F <sub>17</sub>	PFK
	407.7818	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF
	409.7789	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O	HpCDF
	417.8253	M	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> O	HpCDF (S)
	419.8220	M+2	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF (S)
	423.7766	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO <sub>2</sub>	HpCDD
	425.7737	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD
	435.8169	M+2	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO <sub>2</sub>	HpCDD (S)
	437.8140	M+4	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD (S)
	479.7165	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> O	NCPDE
	430.9729	LOCK	C <sub>9</sub> F <sub>17</sub>	PFK
	441.7428	M+2	C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> ClO	OCDF
	443.7399	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDF
	457.7377	M+2	C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> ClO <sub>2</sub>	OCDD
	459.7348	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	OCDD
	469.7779	M+2	<sup>13</sup> C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> ClO <sub>2</sub>	OCDD (S)
	471.7750	M+4	<sup>13</sup> C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	OCDD (S)
	513.6775	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	DCDPE
	442.9728	QC	C <sub>10</sub> F <sub>17</sub>	PFK

[illegible]

The following nuclidic masses were used: H = 1.007825 O = 15.994914 C = 12.000000 <sup>35</sup>Cl = 34.968853  
<sup>13</sup>C = 13.003355 <sup>37</sup>Cl = 36.965903 F = 18.9984 S = Labeled Standard  
 QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

[illegible]

**WARNING**

<sup>b</sup> Used only for <sup>13</sup>C-HpCDF.

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**METHOD 26A - DETERMINATION OF HYDROGEN HALIDE AND  
HALOGEN EMISSIONS FROM STATIONARY SOURCES  
ISOKINETIC METHOD**

**NOTE:** This method does not include all of the specifications (e.g. equipment and supplies) and procedures (e.g. sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

*1.0 Scope and Application.*

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647-01-0
Hydrogen Bromide (HBr)	10035-10-6
Hydrogen Fluoride (HF)	7664-39-3
Chlorine (Cl <sub>2</sub> )	7882-50-5
Bromine (Br <sub>2</sub> )	7726-95-6

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X<sub>2</sub>) [Cl<sub>2</sub> and Br<sub>2</sub>] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those

controlled by wet scrubbers, emitting acid particulate matter (e.g., hydrogen halides dissolved in water droplets).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 *Summary of Method.*

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and fluoride ( $\text{F}^-$ ) ions. The halogens have a very low solubility

in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton ( $H^+$ ), the halide ion, and the hypohalous acid ( $HClO$  or  $HBrO$ ). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

**NOTE:** If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 *Definitions.* [Reserved]

4.0 *Interferences.*

4.1 Volatile materials, such as chlorine dioxide ( $ClO_2$ ) and ammonium chloride ( $NH_4Cl$ ), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen

halide and an hypohalous acid upon dissolution in water. The use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of both HBr and Cl<sub>2</sub> may cause a positive bias in the HCl result with a corresponding negative bias in the Cl<sub>2</sub> result as well as affecting the HBr/Br<sub>2</sub> split.

4.3 High concentrations of nitrogen oxides (NO<sub>x</sub>) may produce sufficient nitrate (NO<sub>3</sub><sup>-</sup>) to interfere with measurements of very low Br<sup>-</sup> levels.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

## 5.0 *Safety.*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0. *Equipment and Supplies.*

**NOTE:** Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26A-1; the apparatus is similar to the Method 5 train where noted as follows:

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, Sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210°C (410°F), a one-piece glass nozzle/liner assembly must be used.

6.1.2 Probe Liner. Same as Method 5, Section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500°C (932°F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120°C (250°F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210°C (410°F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is

saturated with moisture; however, the cyclone is recommended to protect the filter from any liquid droplets present.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

6.1.6 Impinger Train. The following system shall be used to determine the stack gas moisture content and to collect the hydrogen halides and halogens: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger shown in Figure 26A-1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N  $\text{H}_2\text{SO}_4$ . The following two impingers (acid impingers which each contain 100 ml of 0.1 N  $\text{H}_2\text{SO}_4$ ) shall be of the Greenburg-Smith design with the standard tip (Method 5, Section 6.1.1.8). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel)

shall be of the modified Greenburg-Smith design (Method 5, Section 6.1.1.8). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant. Teflon impingers are an acceptable alternative.

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder greater than 120 °C (248 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, (Ascarite II has been found suitable) to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used. The inlet and outlet ends of the tube should be packed with at least 1-cm thickness of glass wool or filter material suitable to prevent escape of fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle following the test run.

6.2 Sample Recovery.

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5, Sections 6.2.1, 6.2.2, 6.2.3, 6.2.4, 6.2.5, and 6.2.7.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel. High-density polyethylene bottles with Teflon screw cap liners to store impinger reagents, 1-liter.

6.2.3 Funnels. Glass or high-density polyethylene, to aid in sample recovery.

### 6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment. To dilute samples to calibration range of the ion chromatograph (IC).

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used.

## 7.0 *Reagents and Standards.*

**NOTE:** Unless otherwise indicated, all reagents must conform to the specifications established by the Committee

on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

#### 7.1 Sampling.

7.1.1 Filter. Teflon mat (e.g., Pallflex TX40HI45) filter. When the stack gas temperature exceeds 210°C (410°F) a quartz fiber filter may be used.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193-77 or 91, Type 3 (incorporated by reference - see § 60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ). To prepare 1 L, slowly add 2.80 ml of concentrated 17.9 M  $\text{H}_2\text{SO}_4$  to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.4 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.5 Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate, ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ).

#### 7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 200 ml of each absorbing solution (250 ml of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water. If a particulate determination is conducted, collect a blank sample of acetone.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110°C (230°F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl<sup>-</sup> concentration using Equation 26A-1 in Section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26A-2 and 26A-3 in Section 12.2, to calculate the Br<sup>-</sup> and F<sup>-</sup> concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate

volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Same as Method 26, Section 7.2.4.

7.2.5 Water. Same as Section 7.1.1.

7.2.6 Acetone. Same as Method 5, Section 7.2.

7.3 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

**NOTE:** The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

#### *8.0 Sample Collection, Preservation, Storage, and Transport.*

**NOTE:** Because of the complexity of this method, testers and analysts should be trained and experienced with the procedures to ensure reliable results.

##### 8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 8.1, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5, Section 8.2.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 8.1.3, except for the following variations: Add 50 ml of 0.1 N  $\text{H}_2\text{SO}_4$  to the condensate impinger, if used. Place 100 ml of 0.1 N  $\text{H}_2\text{SO}_4$  in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last impinger. Set up the train as in Figure 26A-1. When used, the optional cyclone is inserted between the probe liner and filter holder and located in the heated filter box.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check).

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) of greater than  $120^\circ\text{C}$  ( $248^\circ\text{F}$ ) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential underreporting these

emissions. The applicable subparts may specify alternative higher temperatures.) For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-3. If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N  $\text{H}_2\text{SO}_4$ , and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. Before the sampling train integrity is compromised by removing the impinger, conduct a leak-check as described in Method 5, Section 8.4.2.

8.1.6 Post-Test Moisture Removal (Optional). When the optional cyclone is included in the sampling train or when liquid is visible on the filter at the end of a sample run even in the absence of a cyclone, perform the following procedure. Upon completion of the test run, connect the ambient air conditioning tube at the probe inlet and operate the train with the filter heating system at least  $120^\circ\text{C}$  ( $248^\circ\text{F}$ ) at a low flow rate (e.g.,  $\dot{V}_H = 1 \text{ in. H}_2\text{O}$ ) to vaporize any liquid and hydrogen halides in the cyclone or on the filter and pull them through the train into the impingers. After 30 minutes, turn off the flow, remove the conditioning tube, and examine the cyclone and filter for

any visible liquid. If liquid is visible, repeat this step for 15 minutes and observe again. Keep repeating until the cyclone is dry.

**NOTE:** It is critical that this is repeated until the cyclone is completely dry.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap loosely over the tip to prevent gaining or losing particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder. Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the impinger train, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps,

Teflon tape, Parafilm, or aluminum foil may be used to close these openings. Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat samples as follows:

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, Section 8.7.6.1, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, Section 8.7.6.2, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to  $\pm 1$  ml by using a graduated cylinder or by weighing it to  $\pm 0.5$  g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should

be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks to be analyzed with the samples.

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Measure and record the liquid in the alkaline impingers as described in Section 8.2.3. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf). Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank to be analyzed with the samples.

**NOTE:** 25 mg per sodium thiosulfate per ppm halogen anticipated to be in the stack includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second  $\text{Cl}^-$  ion in the alkaline solution.

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, Section 8.7.6.3, *Container No. 3.*

## 8.2.6 Container Nos. 6 through 9 (Reagent Blanks).

Save portions of the absorbing reagents (0.1 N  $\text{H}_2\text{SO}_4$  and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, prelabeled sample container.

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

## 9.0 *Quality Control.*

### 9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
8.1.4, 10.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate, sample volume
11.5	Audit sample analysis	Evaluate analyst's technique and standards preparation

9.1 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 *Calibration and Standardization.*

**NOTE:** Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, Sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

### 10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H<sub>2</sub>SO<sub>4</sub> or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing

the three stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in  $\mu\text{g/ml}$ .

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

### *11.0 Analytical Procedures.*

**NOTE:** the liquid levels in the sample containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to

the approval of the Administrator, to correct the final results.

#### 11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50  $\mu$ l sample loop, and a conductivity detector set on 1.0  $\mu$ S full scale is shown in Figure 26-2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{F}^-$  appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to Section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  peaks. Use the mean response of the duplicate injections to

determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicator injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2 Container Nos. 1 and 2 and Acetone Blank (Optional; Particulate Determination). Same as Method 5, Sections 11.2.1 and 11.2.2, respectively.

11.3 Container No. 5. Same as Method 5, Section 11.2.3 for silica gel.

11.4 Audit Sample Analysis.

11.4.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two EPA audit samples must be analyzed, subject to availability.

11.4.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

11.4.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met,

duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

#### 11.5 Audit Sample Results.

11.5.1 Calculate the concentrations in mg/L of audit sample and submit results following the instructions provided with the audit samples.

11.5.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.5.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.5.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the

Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

#### 12.0. *Data Analysis and Calculations.*

**NOTE:** Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

##### 12.1 Nomenclature. Same as Method 5, Section 12.1.

In addition:

$B_{X^-}$  = Mass concentration of applicable absorbing solution blank,  $\mu\text{g}$  halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ )/ml, not to exceed 1  $\mu\text{g}/\text{ml}$  which is 10 times the published analytical detection limit of 0.1  $\mu\text{g}/\text{ml}$ . (It is also approximately 5 percent of the mass concentration anticipated to result from a one hour sample at 10 ppmv  $\text{HCl}$ .)

$C$  = Concentration of hydrogen halide ( $\text{HX}$ ) or halogen ( $\text{X}_2$ ), dry basis,  $\text{mg}/\text{dscm}$ .

$K$  =  $10^{-3} \text{ mg}/\mu\text{g}$ .

$K_{\text{HCl}}$  =  $1.028 (\mu\text{g HCl}/\mu\text{g-mole})/(\mu\text{g Cl}^-/\mu\text{g-mole})$ .

$$K_{\text{HBr}} = 1.013 (\mu\text{g HBr}/\mu\text{g-mole})/(\mu\text{g Br}^-/\mu\text{g-mole}).$$

$$K_{\text{HF}} = 1.053 (\mu\text{g HF}/\mu\text{g-mole})/(\mu\text{g F}^-/\mu\text{g-mole}).$$

$$m_{\text{HX}} = \text{Mass of HCl, HBr, or HF in sample, } \mu\text{g}.$$

$$m_{\text{X}_2} = \text{Mass of Cl}_2 \text{ or Br}_2 \text{ in sample, } \mu\text{g}.$$

$$S_{\text{X}^-} = \text{Analysis of sample, } \mu\text{g halide ion (Cl}^-, \text{Br}^-, \text{F}^-)/\text{ml}.$$

$$V_{\text{s}} = \text{Volume of filtered and diluted sample, ml}.$$

12.2 Calculate the exact  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  concentration in the halide salt stock standard solutions using the following equations.

$$\mu\text{g Cl}^-/\text{ml} = \text{g of NaCl} \times 10^3 \times 35.453/58.44 \quad \text{Eq. 26A-1}$$

$$\mu\text{g Br}^-/\text{ml} = \text{g of NaBr} \times 10^3 \times 79.904/102.90 \quad \text{Eq. 26A-2}$$

$$\mu\text{g F}^-/\text{ml} = \text{g of NaF} \times 10^3 \times 18.998/41.99 \quad \text{Eq. 26A-3}$$

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5-3 of Method 5).

12.4 Dry Gas Volume. Calculate  $V_{\text{m(std)}}$  and adjust for leakage, if necessary, using the equation in Section 12.3 of Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor  $V_{\text{w(std)}}$  and moisture content  $B_{\text{ws}}$  from the data obtained in this method (Figure 5-3 of Method 5); use Equations 5-2 and 5-3 of Method 5.

## 12.6 Isokinetic Variation and Acceptable Results.

Use Method 5, Section 12.11.

12.7 Acetone Blank Concentration, Acetone Wash Blank Residue Weight, Particulate Weight, and Particulate Concentration. For particulate determination.

12.8 Total  $\mu\text{g}$  HCl, HBr, or HF Per Sample.

$$m_{\text{HX}} = K_{\text{HCl, HBr, HF}} V_s (S_{\text{X}^-} - B_{\text{X}^-}) \quad \text{Eq. 26A-4}$$

12.9 Total  $\mu\text{g}$   $\text{Cl}_2$  or  $\text{Br}_2$  Per Sample.

$$m_{\text{X}_2} = V_s (S_{\text{X}^-} - B_{\text{X}^-}) \quad \text{Eq. 26A-5}$$

12.10 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{\text{HX, X}_2} / V_{\text{m(std)}} \quad \text{Eq. 26A-6}$$

## 12.11 Stack Gas Velocity and Volumetric Flow Rate.

Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 12.3 and 12.4 of Method 2.

## 3.0 Method Performance.

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl perhaps due to reaction with small amounts of moisture in the probe and filter. Similar bias for the other hydrogen halides is possible.

13.2 Sample Stability. The collected  $\text{Cl}^-$  samples can be stored for up to 4 weeks for analysis for HCl and  $\text{Cl}_2$ .

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2  $\mu\text{g/ml}$ . Detection limits for the other analyses should be similar. Assuming 300 ml of liquid recovered for the acidified impingers and a similar amounts recovered from the basic impingers, and 1 dscm of stack gas sampled, the analytical detection limits in the stack gas would be about 0.04 ppm for HCl and Cl<sub>2</sub>, respectively.

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References.*

1. Steinsberger, S. C. and J. H. Margeson.  
Laboratory and Field Evaluation of a Methodology for  
Determination of Hydrogen Chloride Emissions from Municipal  
and Hazardous Waste Incinerators. U.S. Environmental  
Protection Agency, Office of Research and Development.  
Publication No. 600/3-89/064. April 1989. Available from  
National Technical Information Service, Springfield, VA  
22161 as PB89220586/AS.

2. State of California Air Resources Board. Method  
421 - Determination of Hydrochloric Acid Emissions from  
Stationary Sources. March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in  
the Methodology for Measuring Hydrochloric Acid in  
Combustion Source Emissions. J. Environ. Sci. Health.  
A19(3): 337-350. 1984.

4. Stern, D.A., B.M. Myatt, J.F. Lachowski, and K.T.  
McGregor. Speciation of Halogen and Hydrogen Halide  
Compounds in Gaseous Emissions. In: Incineration and  
Treatment of Hazardous Waste: Proceedings of the 9th Annual  
Research Symposium, Cincinnati, Ohio, May 2-4, 1983.  
Publication No. 600/9-84-015. July 1984. Available from

National Technical Information Service, Springfield, VA  
22161 as PB84-234525.

5. Holm, R.D. and S.A. Barksdale. Analysis of Anions  
in Combustion Products. In: Ion Chromatographic Analysis  
of Environmental Pollutants, E. Sawicki, J.D. Mulik, and  
E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor  
Science Publishers. 1978. pp. 99-110.

*17.0 Tables, Diagrams, Flowcharts, and Validation Data.*

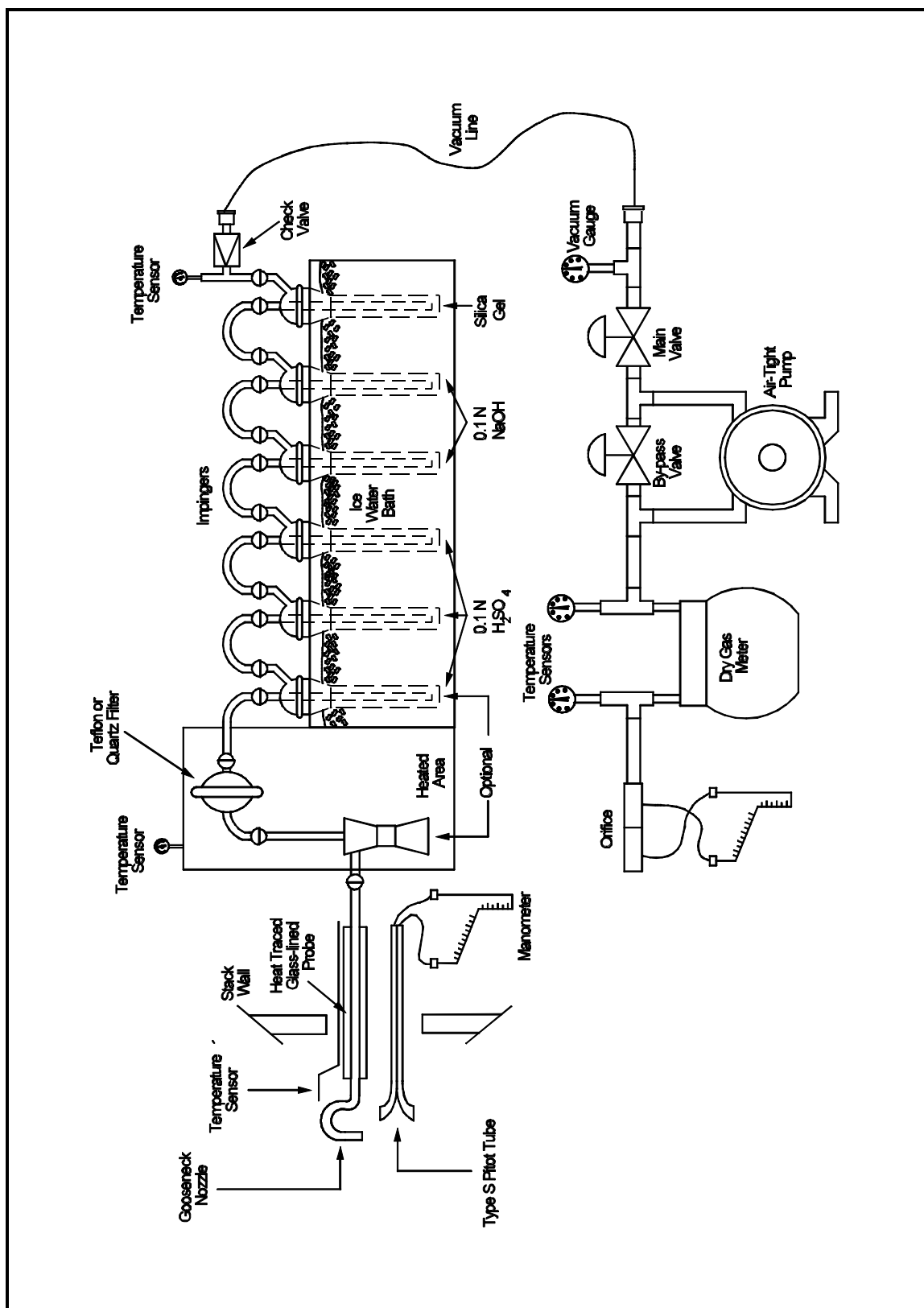


Figure 26A-1. Sampling Train

## METHOD 29 - DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

**NOTE:** This method does not include all of the specifications (e.g. equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

### *1.0 Scope and Application.*

#### 1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4

Analyte	CAS No.
Thallium (Tl)	7440-28-0
Zinc (Zn)	7440-66-6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

## 2.0 Summary of Method.

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy (CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy

(ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

### 3.0 *Definitions.* [Reserved]

### 4.0 *Interferences.*

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in Section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

## 5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid ( $\text{HNO}_3$ ). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of

the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs. 30% H<sub>2</sub>O<sub>2</sub> is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate (KMnO<sub>4</sub>). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the acidic  $\text{KMnO}_4$  absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

#### *6.0 Equipment and Supplies.*

6.1 Sampling. A schematic of the sampling train is shown in Figure 29-1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one

chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, Section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, Section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, Section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified  $\text{KMnO}_4$ ) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within  $1^\circ\text{C}$  ( $2^\circ\text{F}$ ) at the

outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, Sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see Section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified  $\text{KMnO}_4$ -containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves.

For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml.

For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in Section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10°C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in Section 16.0. See **NOTE 2:** Section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in Section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer. Same as EPA Method 6020 in Reference 2 in Section 16.0.

## 7.0 *Reagents and Standards.*

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by

the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

## 7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than  $1.3 \mu\text{g}/\text{in.}^2$  of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide ( $\text{SO}_2$ ) or sulfur trioxide ( $\text{SO}_3$ ) shall be as described in Section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193-77 or 91, Type II (incorporated by reference -- see §60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3  $\text{HNO}_3$ , Concentrated. Baker Instra-analyzed or equivalent.

7.2.4  $\text{HCl}$ , Concentrated. Baker Instra-analyzed or equivalent.

7.2.5  $\text{H}_2\text{O}_2$ , 30 Percent (V/V).

7.2.6  $\text{KMnO}_4$ .

7.2.7  $\text{H}_2\text{SO}_4$ , Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 7.1.2 and 7.1.4, respectively.

### 7.3 Pretest Preparation of Sampling Reagents.

7.3.1  $\text{HNO}_3/\text{H}_2\text{O}_2$  Absorbing Solution, 5 Percent  $\text{HNO}_3$ /10 Percent  $\text{H}_2\text{O}_2$ . Add carefully with stirring 50 ml of concentrated  $\text{HNO}_3$  to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent  $\text{H}_2\text{O}_2$ . Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic  $\text{KMnO}_4$  Absorbing Solution, 4 Percent  $\text{KMnO}_4$  (W/V), 10 Percent  $\text{H}_2\text{SO}_4$  (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated  $\text{H}_2\text{SO}_4$  into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent  $\text{H}_2\text{SO}_4$  (V/V). Dissolve, with stirring, 40 g of  $\text{KMnO}_4$  into 10 percent  $\text{H}_2\text{SO}_4$  (V/V) and add 10 percent  $\text{H}_2\text{SO}_4$  (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

**Precaution:** To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3  $\text{HNO}_3$ , 0.1 N. Add with stirring 6.3 ml of concentrated  $\text{HNO}_3$  (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.4  $\text{HCl}$ , 8 N. Carefully add with stirring 690 ml of concentrated  $\text{HCl}$  to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

#### 7.4 Glassware Cleaning Reagents.

7.4.1  $\text{HNO}_3$ , Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3  $\text{HNO}_3$ , 10 Percent (V/V). Add with stirring 500 ml of concentrated  $\text{HNO}_3$  to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid

chemicals as described in Reference 3 in Section 16.0.

Refer to References 1, 2, or 5 in Section 16.0 for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to Section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO<sub>3</sub>, Concentrated. Baker Instra-analyzed or equivalent.

7.5.4 HNO<sub>3</sub>, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO<sub>3</sub> to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO<sub>3</sub>, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO<sub>3</sub> to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 In Section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in Section 16.0 for preparation.

7.5.9 KMnO<sub>4</sub>, 5 Percent (W/V). See Reference 2 in Section 16.0 for preparation.

7.5.10  $\text{H}_2\text{SO}_4$ , Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in Section 16.0 for preparation.

7.5.12 Nickel Nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

7.5.13 Lanthanum Oxide,  $\text{La}_2\text{O}_3$ .

7.5.14 Hg Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.15 Pb Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.16 As Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.17 Cd Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.18 Cr Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.19 Sb Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.20 Ba Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.21 Be Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.22 Co Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.23 Cu Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.24 Mn Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.25 Ni Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.26 P Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.27 Se Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.28 Ag Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.29 Tl Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.30 Zn Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.31 Al Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

7.5.32 Fe Standard (AAS Grade), 1000  $\mu\text{g}/\text{ml}$ .

### 7.5.33 Hg Standards and Quality Control Samples.

Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO<sub>3</sub> and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent KMnO<sub>4</sub>, 5 ml of 15 percent HNO<sub>3</sub>, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

### 7.5.34 ICAP Standards and Quality Control Samples.

Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

#### MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn

II	Ba, Co, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

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Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO<sub>3</sub>. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO<sub>3</sub>. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask,

and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

#### 7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of  $\text{La}_2\text{O}_3$  in 10 ml of concentrated  $\text{HNO}_3$ , and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal

amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

## *8.0 Sample Collection, Preservation, Transport, and Storage.*

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water, rinse a final time with acetone, and allow to air

dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, Section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29-1. Follow the same general procedures given in Method 5, Section 8.3, except place 100 ml of the  $\text{HNO}_3/\text{H}_2\text{O}_2$  solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29-1. Place 100 ml of the acidic  $\text{KMnO}_4$  absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29-1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29-1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use

Teflon tape or other non-contaminating material instead of silicone grease.

**Precaution:** Exercise extreme care to prevent contamination within the train. Prevent the acidic  $\text{KMnO}_4$  from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic  $\text{H}_2\text{O}_2$  from mixing with the acidic  $\text{KMnO}_4$ .

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 8.4.2 (Pretest Leak-Check), Section 8.4.3 (Leak-Checks During the Sample Run), and Section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 8.5. When sampling for Hg, use a procedure analogous to that described in Section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5-3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The

probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon® tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29-2a and 29-2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting,

probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt

acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N  $\text{HNO}_3$ , and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, Section 8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

**NOTE:** The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used,  $\text{HNO}_3/\text{H}_2\text{O}_2$  Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the

moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N  $\text{HNO}_3$  using the procedure as applicable in Method 12, Section 8.7.3.

**NOTE:** The use of exactly 100 ml of 0.1 N  $\text{HNO}_3$  rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N  $\text{HNO}_3$ ), 5B ( $\text{KMnO}_4/\text{H}_2\text{SO}_4$  absorbing solution), and 5C (8 N  $\text{HCl}$  rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N  $\text{HNO}_3$  and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this

acidic  $\text{KMnO}_4$  solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified  $\text{KMnO}_4$  solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the **Precaution:** in Section 7.3.2.

**NOTE:** Due to the potential reaction of  $\text{KMnO}_4$  with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70-72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 If no visible deposits remain after the water rinse, no further rinse is necessary. However, if deposits remain on the impinger surfaces, wash them with 25 ml of 8 N  $\text{HCl}$ , and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200

ml of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N  $\text{HNO}_3$  Blank). At least once during each field test, place 300 ml of the 0.1 N  $\text{HNO}_3$  solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent  $\text{HNO}_3$ /10 Percent  $\text{H}_2\text{O}_2$  Blank). At least once during each field test, place 200 ml of the 5 Percent  $\text{HNO}_3$ /10 Percent  $\text{H}_2\text{O}_2$  solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified  $\text{KMnO}_4$  Blank). At least once during each field test, place 100 ml of the acidified  $\text{KMnO}_4$  solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in Section 8.2.9.2.

Read the **Precaution:** in Section 7.3.2 and read the **NOTE** in Section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29-3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in Section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated  $\text{HNO}_3$  and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at  $140^\circ\text{C}$  ( $285^\circ\text{F}$ ) for 6 hours. Then cool the samples to room temperature, and combine with the acid digested probe rinse as required in Section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in Section 8.3.1.2

and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated  $\text{HNO}_3$ . Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated  $\text{HNO}_3$  to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the

sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated  $\text{HNO}_3$ , 4 ml of concentrated HF, and then continuing to follow the procedures described in Section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 8.3.1.2. The resultant combined sample is referred to as "Sample Fraction 1". Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is "Analytical Fraction 1". Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as "Analytical Fraction 1B". Label the remaining 250-ml portion as "Analytical Fraction 1A". Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample to within 0.5 ml and label it "Sample Fraction 2". Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot "Analytical Fraction 2B". Label the remaining portion of Container

No. 4 as "Sample Fraction 2A". Sample Fraction 2A defines the volume of Analytical Fraction 2A prior to digestion. All of Sample Fraction 2A is digested to produce "Analytical Fraction 2A". Analytical Fraction 2A defines the volume of Sample Fraction 2A after its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated  $\text{HNO}_3$  by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent  $\text{HNO}_3$ , and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent  $\text{H}_2\text{O}_2$  and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent  $\text{HNO}_3$  and heat for 6 minutes total heating time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent  $\text{H}_2\text{O}_2$  and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

**NOTE:** All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be Analytical Fraction 3A. To remove any brown  $\text{MnO}_2$  precipitate from the contents of Container No. 5B, filter its contents through Whatman 40

filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown  $\text{MnO}_2$  precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown  $\text{MnO}_2$  precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the  $\text{MnO}_2$ , add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown  $\text{MnO}_2$  from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 *Quality Control.*

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in Sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per Section 8.3.1, 100 ml from Container No. 7 per Section 8.3.2, and 100 ml from Container No. 8A per Section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per Section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in Section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown  $\text{MnO}_2$  precipitate from the blank for Analytical Fraction 3B by the same procedure as described in Section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per Section 11.1.1 and/or Section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per Section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in Section 8 of Methods 6010

and 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the

accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in Standard Methods for Water and Wastewater Method 303F.

#### *10.0 Calibration and Standardization.*

**NOTE:** Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent,

perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer - Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in Section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

#### *11.0 Analytical Procedure.*

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29-3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the

digested samples from the front-half of the train.

Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in Sections 11.1.1 and 11.1.2, respectively.

Analytical Fraction 1B is for front-half Hg analysis as described in Section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and  $\text{HNO}_3/\text{H}_2\text{O}_2$  impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the  $\text{H}_2\text{SO}_4/\text{KMnO}_4$  Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in Section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method

200.7. Follow the quality control procedures described in Section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29-2. These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

**NOTE:** When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29-3 to determine which techniques and procedures to apply for each target metal. Use Table 29-3, if necessary, to

determine techniques for minimization of interferences. Calibrate the instrument according to Section 10.3 and follow the quality control procedures specified in Section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F, or, optionally using **NOTE No. 2** at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see **NOTE No. 1** at end of this section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100

ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See **NOTE No. 2** at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent  $\text{HNO}_3$  (1.5 ml concentrated  $\text{HNO}_3$  per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15  $\text{HNO}_3$  percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

**NOTE No. 1:** When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29-1, select a 10 ml aliquot for digestion and analysis as described.

**NOTE No. 2:** Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two

steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

## *12.0 Data Analysis and Calculations.*

### 12.1 Nomenclature.

- A = Analytical detection limit,  $\mu\text{g/ml}$ .
- B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
- C = Stack sample gas volume,  $\text{dscm}^3$ .
- $C_{a1}$  = Concentration of metal in Analytical Fraction 1A as read from the standard curve,  $\mu\text{g/ml}$ .
- $C_{a2}$  = Concentration of metal in Analytical Fraction 2A as read from the standard curve, ( $\mu\text{g/ml}$ ).
- $C_s$  = Concentration of a metal in the stack gas,  $\text{mg/dscm}$ .

- D = In-stack detection limit,  $\mu\text{g}/\text{m}^3$ .
- $F_a$  = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see Section 8.3.4.)
- $F_d$  = Dilution factor ( $F_d$  = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading  $C_{a1}$ . For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range,  $F_d = 5$ ).
- $\text{Hg}_{bh}$  = Total mass of Hg collected in the back-half of the sampling train,  $\mu\text{g}$ .
- $\text{Hg}_{bh2}$  = Total mass of Hg collected in Sample Fraction 2,  $\mu\text{g}$ .
- $\text{Hg}_{bh3(A,B,C)}$  = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C,  $\mu\text{g}$ .
- $\text{Hg}_{bhb}$  = Blank correction value for mass of Hg detected in back-half field reagent blanks,  $\mu\text{g}$ .
- $\text{Hg}_{fh}$  = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1),  $\mu\text{g}$ .

- $Hg_{fhh}$  = Blank correction value for mass of Hg detected in front-half field reagent blank,  $\mu g$ .
- $Hg_t$  = Total mass of Hg collected in the sampling train,  $\mu g$ .
- $M_{bh}$  = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2),  $\mu g$ .
- $M_{bhb}$  = Blank correction value for mass of metal detected in back-half field reagent blank,  $\mu g$ .
- $M_{fh}$  = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1),  $\mu g$ .
- $M_{fhh}$  = Blank correction value for mass of metal detected in front-half field reagent blank,  $\mu g$ .
- $M_t$  = Total mass of each metal (separately stated for each metal) collected in the sampling train,  $\mu g$ .
- $M_t$  = Total mass of that metal collected in the sampling train,  $\mu g$ ; (substitute  $Hg_t$  for  $M_t$  for the Hg calculation).
- $Q_{bh2}$  = Quantity of Hg,  $\mu g$ , TOTAL in the ALIQUOT of Analytical Fraction 2B selected for

digestion and analysis . **NOTE:** For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to Section 11.1.3 and its **NOTES** Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for  $Q_{bh2}$ .

$Q_{bh3(A,B,C)}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis (see **NOTES** in Sections 12.7.1 and 12.7.2 describing the quantity "Q" and calculate similarly).

$Q_{fh}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis . **NOTE:** For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 11.1.3 and its **NOTES** Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for  $Q_{fh}$ .

$V_a$  = Total volume of digested sample solution (Analytical Fraction 2A), ml (see

Section 8.3.4.1 or 8.3.4.2, as applicable).

$V_{f1B}$  = Volume of aliquot of Analytical Fraction 1B analyzed, ml. **NOTE:** For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent  $\text{HNO}_3$  as described in Section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to Section 11.1.3 and analyzed,  $V_{f1B}$  would be 0.02 ml.

$V_{f2B}$  = Volume of Analytical Fraction 2B analyzed, ml. **NOTE:** For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent  $\text{HNO}_3$  as described in Section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed,  $V_{f2B}$  would be 0.5 ml.

$V_{f3(A,B,C)}$  = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in Sections 12.7.1 and 12.7.2, describing the quantity "V" and calculate similarly).

$V_{m(std)}$  = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$  = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$  = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$  = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$  = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4$  =  $10^{-3}$  mg/ $\mu$ g.

12.2 Dry Gas Volume. Using the data from this test, calculate  $V_{m(std)}$ , the dry gas sample volume at standard conditions as outlined in Section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor  $V_{w(std)}$  and the moisture content  $B_{ws}$  of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29-4 using the conditions described in Section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \quad \text{Eq. 29-1}$$

## 12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{a1} F_d V_{soln,1} \quad \text{Eq. 29-2}$$

**NOTE:** If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29-2 through 29-4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \quad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \quad \text{Eq. 29-4}$$

**NOTE:** If the measured blank value for the front half ( $M_{f_{hb}}$ ) is in the range 0.0 to "A"  $\mu\text{g}$  [where "A"  $\mu\text{g}$  equals the value determined by multiplying 1.4  $\mu\text{g}/\text{in.}^2$  times the actual area in  $\text{in.}^2$  of the sample filter], use  $M_{f_{hb}}$  to correct the emission sample value ( $M_{f_{h}}$ ); if  $M_{f_{hb}}$  exceeds "A"  $\mu\text{g}$ , use the greater of I or II:

I. "A"  $\mu\text{g}$ .

II. the lesser of (a)  $M_{f_{hb}}$ , or (b) 5 percent of  $M_{f_{h}}$ .

If the measured blank value for the back-half ( $M_{b_{hb}}$ ) is in the range 0.0 to 1  $\mu\text{g}$ , use  $M_{b_{hb}}$  to correct the emission sample value ( $M_{b_{h}}$ ); if  $M_{b_{hb}}$  exceeds 1  $\mu\text{g}$ , use the greater of I or II:

I. 1  $\mu\text{g}$ .

II. the lesser of (a)  $M_{b_{hb}}$ , or (b) 5 percent of  $M_{b_{h}}$ .

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg.

Calculate the amount of Hg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29-5:

$$\text{Hg}_{f_{h}} = \frac{Q_{f_{h}}}{V_{f1B}} (V_{\text{soln},1}) \quad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29-6:

$$\text{Hg}_{\text{bh2}} = \frac{Q_{\text{bh2}}}{V_{\text{f2B}}} (V_{\text{soln},2}) \quad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29-7:

$$\text{Hg}_{\text{bh3(A,B,C)}} = \frac{Q_{\text{bh3(A,B,C)}}}{V_{\text{f3(A,B,C)}}} (V_{\text{soln},3(\text{A,B,C},)}) \quad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29-8:

$$\text{Hg}_{\text{bh}} = \text{Hg}_{\text{bh2}} + \text{Hg}_{\text{bh3A}} + \text{Hg}_{\text{bh3B}} + \text{Hg}_{\text{bh3C}} \quad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29-9:

$$\text{Hg}_{\text{t}} = (\text{Hg}_{\text{fh}} - \text{Hg}_{\text{fhh}}) + (\text{Hg}_{\text{bh}} - \text{Hg}_{\text{bhbb}}) \quad \text{Eq. 29-9}$$

**NOTE:** If the total of the measured blank values ( $\text{Hg}_{\text{fhh}} + \text{Hg}_{\text{bhbb}}$ ) is in the range of 0.0 to 0.6  $\mu\text{g}$ , then use the total to correct the sample value ( $\text{Hg}_{\text{fh}} + \text{Hg}_{\text{bh}}$ ); if it exceeds 0.6  $\mu\text{g}$ , use the greater of I. or II:

I. 0.6  $\mu\text{g}$ .

II. the lesser of (a)  $(Hg_{fhh} + Hg_{bhh})$ , or (b) 5 percent of the sample value  $(Hg_{fh} + Hg_{bh})$ .

#### 12.8 Individual Metal Concentrations in Stack Gas.

Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29-10:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \quad \text{Eq. 29-10}$$

#### 12.9 Isokinetic Variation and Acceptable Results.

Same as Method 5, Sections 12.11 and 12.12, respectively.

#### 13.0 Method Performance.

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml ( $\mu\text{g/ml}$ ) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50  $\mu\text{g/ml}$  As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20  $\mu\text{g/ml}$  of Cd should be diluted to that level before analysis.

#### 13.2 Analytical Detection Limits.

**NOTE:** See Section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on SW-846, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follow: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the digestion of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used.

13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

### 13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) the procedures described in this method, (2) the analytical detection limits described in Section 13.2 and in SW-846, (3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m<sup>3</sup>. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29-1 and were calculated by using Eq. 29-1 shown in Section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source

test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29-1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of Hg only, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m<sup>3</sup>. If the sampling time is increased to four hours and 5 m<sup>3</sup> are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29-1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical

Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in Sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development

test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

*14.0 Pollution Prevention.* [Reserved]

*15.0 Waste Management.* [Reserved]

*16.0 References.*

1. Method 303F in Standard Methods for the Examination of Water Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

*17.0 Tables, Diagrams, Flowcharts, and Validation Data.*

**TABLE 29-1. IN-STACK METHOD DETECTION LIMITS ( $\mu\text{g}/\text{m}^3$ )  
FOR THE FRONT-HALF, THE BACK-HALF, AND THE  
TOTAL SAMPLING TRAIN USING ICAP, GFAAS, AND CVAAS.**

Metal	Front-half: Probe and Filter	Back-half: Impingers 1-3	Back-half: Impingers 4-6 <sup>a</sup>	Total Train:
Antimony	<sup>1</sup> 7.7 (0.7)	<sup>1</sup> 3.8 (0.4)		<sup>1</sup> 11.5 (1.1)
Arsenic	<sup>1</sup> 12.7 (0.3)	<sup>1</sup> 6.4 (0.1)		<sup>1</sup> 19.1 (0.4)
Barium	0.5	0.3		0.8
Beryllium	<sup>1</sup> 0.07 (0.05)	<sup>1</sup> 0.04 (0.03)		<sup>1</sup> 0.11 (0.08)
Cadmium	<sup>1</sup> 1.0 (0.02)	<sup>1</sup> 0.5 (0.01)		<sup>1</sup> 1.5 (0.03)
Chromium	<sup>1</sup> 1.7 (0.2)	<sup>1</sup> 0.8 (0.1)		<sup>1</sup> 2.5 (0.3)
Cobalt	<sup>1</sup> 1.7 (0.2)	<sup>1</sup> 0.8 (0.1)		<sup>1</sup> 2.5 (0.3)
Copper	1.4	0.7		2.1
Lead	<sup>1</sup> 10.1 (0.2)	<sup>1</sup> 5.0 (0.1)		<sup>1</sup> 15.1 (0.3)
Manganese	<sup>1</sup> 0.5 (0.2)	<sup>1</sup> 0.2 (0.1)		<sup>1</sup> 0.7 (0.3)
Mercury	<sup>2</sup> 0.06	<sup>2</sup> 0.3	<sup>2</sup> 0.2	<sup>2</sup> 0.56
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	<sup>1</sup> 18 (0.5)	<sup>1</sup> 9 (0.3)		<sup>1</sup> 27 (0.8)
Silver	1.7	0.9 (0.7)		2.6
Thallium	<sup>1</sup> 9.6 (0.2)	<sup>1</sup> 4.8 (0.1)		<sup>1</sup> 14.4 (0.3)
Zinc	0.5	0.3		0.8

<sup>a</sup>Mercury analysis only.

<sup>1</sup>Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see Section 11.1.2).

<sup>2</sup>Detection limit when analyzed by CVAAS, estimated for Back-half and Total Train. See Sections 13.2 and 11.1.3.

Note: Actual method in-stack detection limits may vary from these values, as described in Section 13.3.3.

**TABLE 29-2. RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS**

Analyte	Wavelength (nm)
Aluminum (Al)	308.215
Antimony (Sb)	206.833
Arsenic (As)	193.696
Barium (Ba)	455.403
Beryllium (Be)	313.042
Cadmium (Cd)	226.502
Chromium (Cr)	267.716
Cobalt (Co)	228.616
Copper (Cu)	328.754
Iron (Fe)	259.940
Lead (Pb)	220.353
Manganese (Mn)	257.610
Nickel (Ni)	231.604
Phosphorus (P)	214.914
Selenium (Se)	196.026
Silver (Ag)	328.068
Thallium (Tl)	190.864
Zinc (Zn)	213.856

**TABLE 29-3. APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS.**

Metal	Technique	SW-846 <sup>1</sup> Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 µl of phosphorus acid to 1 ml of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr	Background correction required Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insoluble	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample and standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination	Strontium removes Cu and phosphate Great care taken to avoid contamination

TABLE 29-3. Continued.

Metal	Technique	SW-846 <sup>1</sup> Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb, Ni, Cu, or acid	Use secondary wavelength of 231.1 nm; match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic Volatilization Aluminum	Spike samples and add nickel nitrate solution to digestates prior to analysis Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium  Barium Ionization	High hollow cathode current and narrow band set 2 ml of KCl per 100 ml of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg and Si	Add 0.1% fluoride
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption and light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess Chloride Pipet Tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards-- Consult mfgs' literature
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a known constant effect and to eliminate effect of phosphate
Cu	Aspiration	7210	324.7	Absorption and Scatter	Consult manufacturer's manual

<sup>1</sup>Refer to EPA publication SW-846 (Reference 2 in Section 16.0).

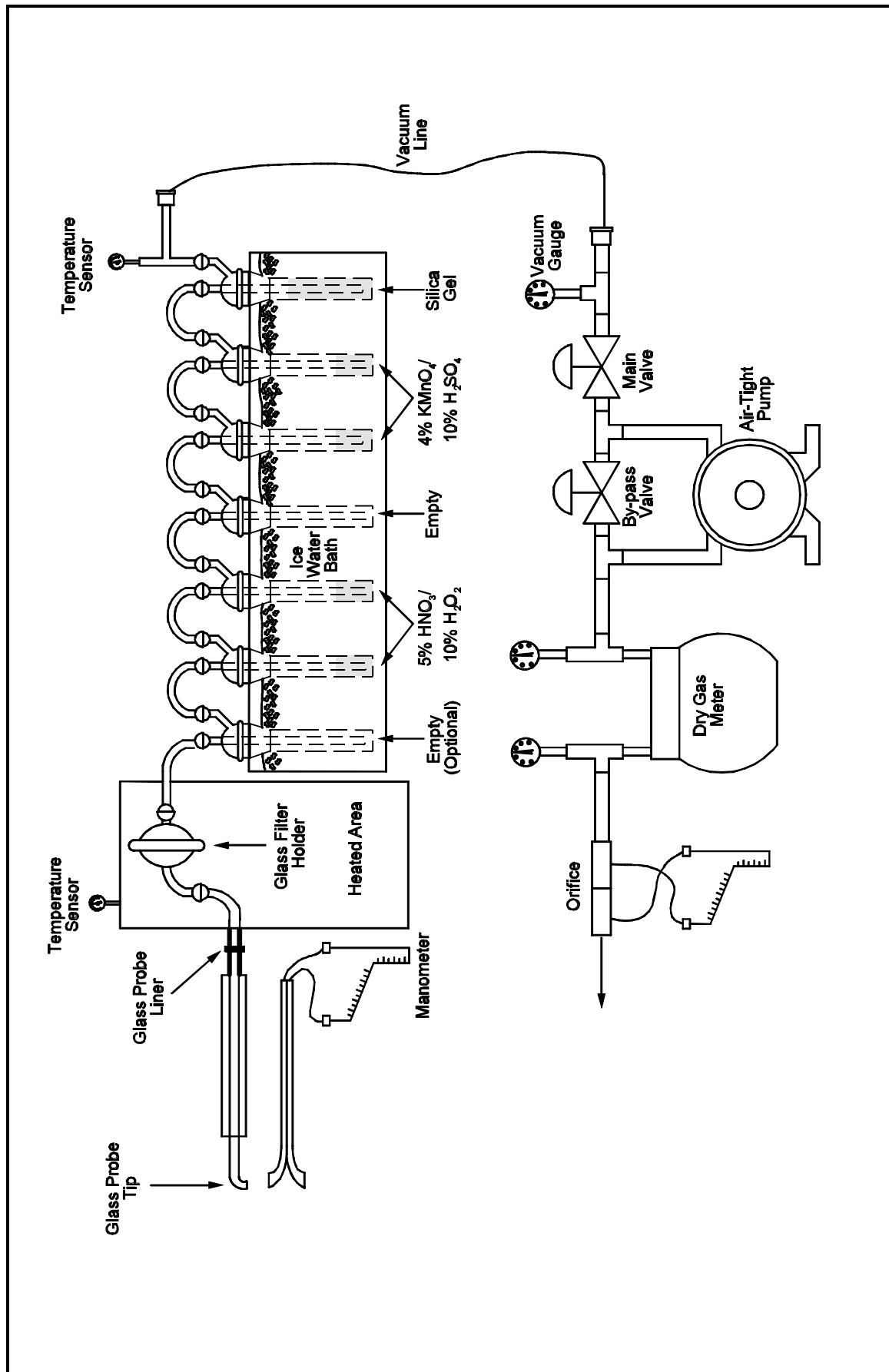


Figure 29-1. Sampling Train.

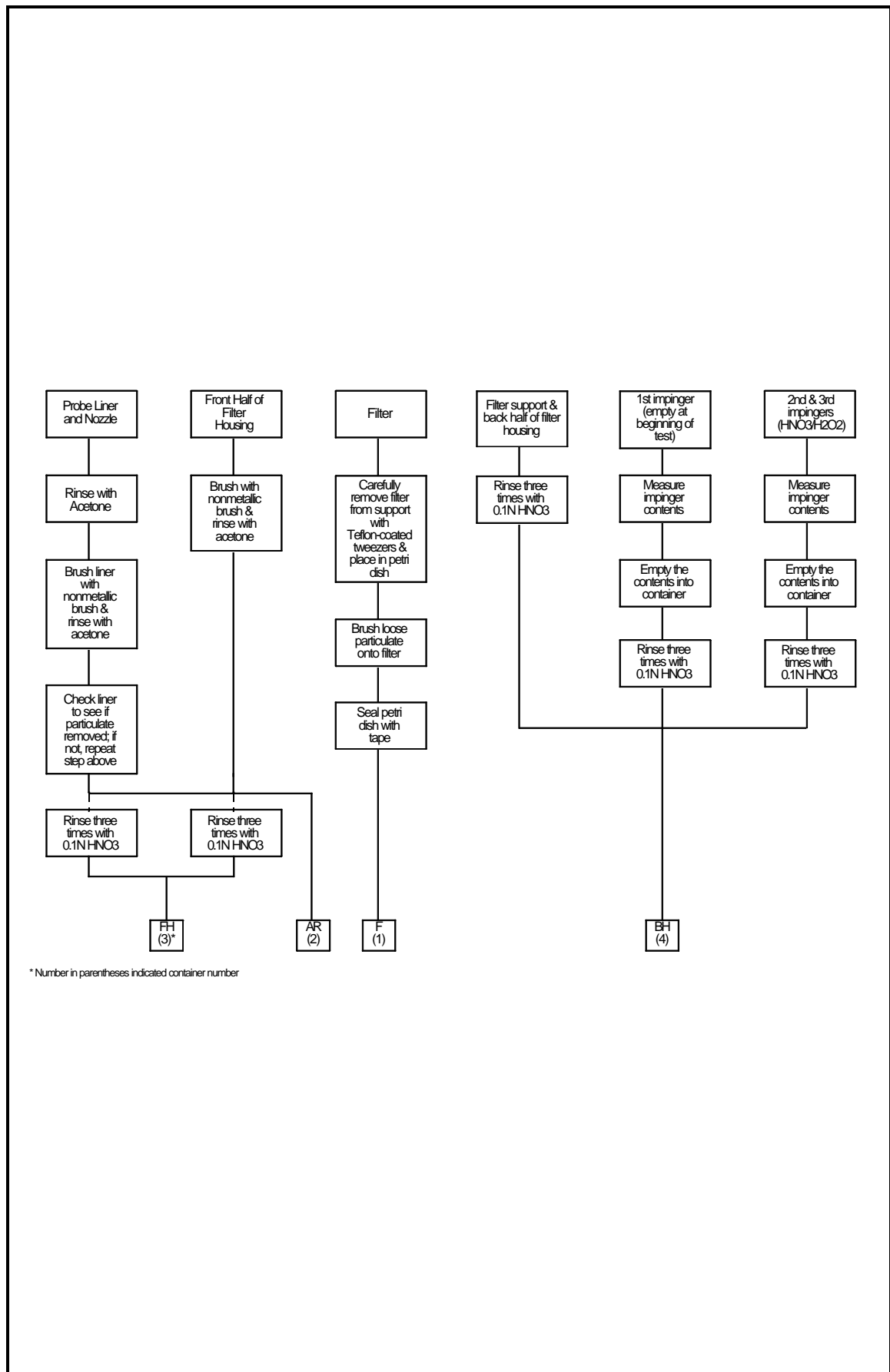


Figure 29-2a. Sample Recovery Scheme.

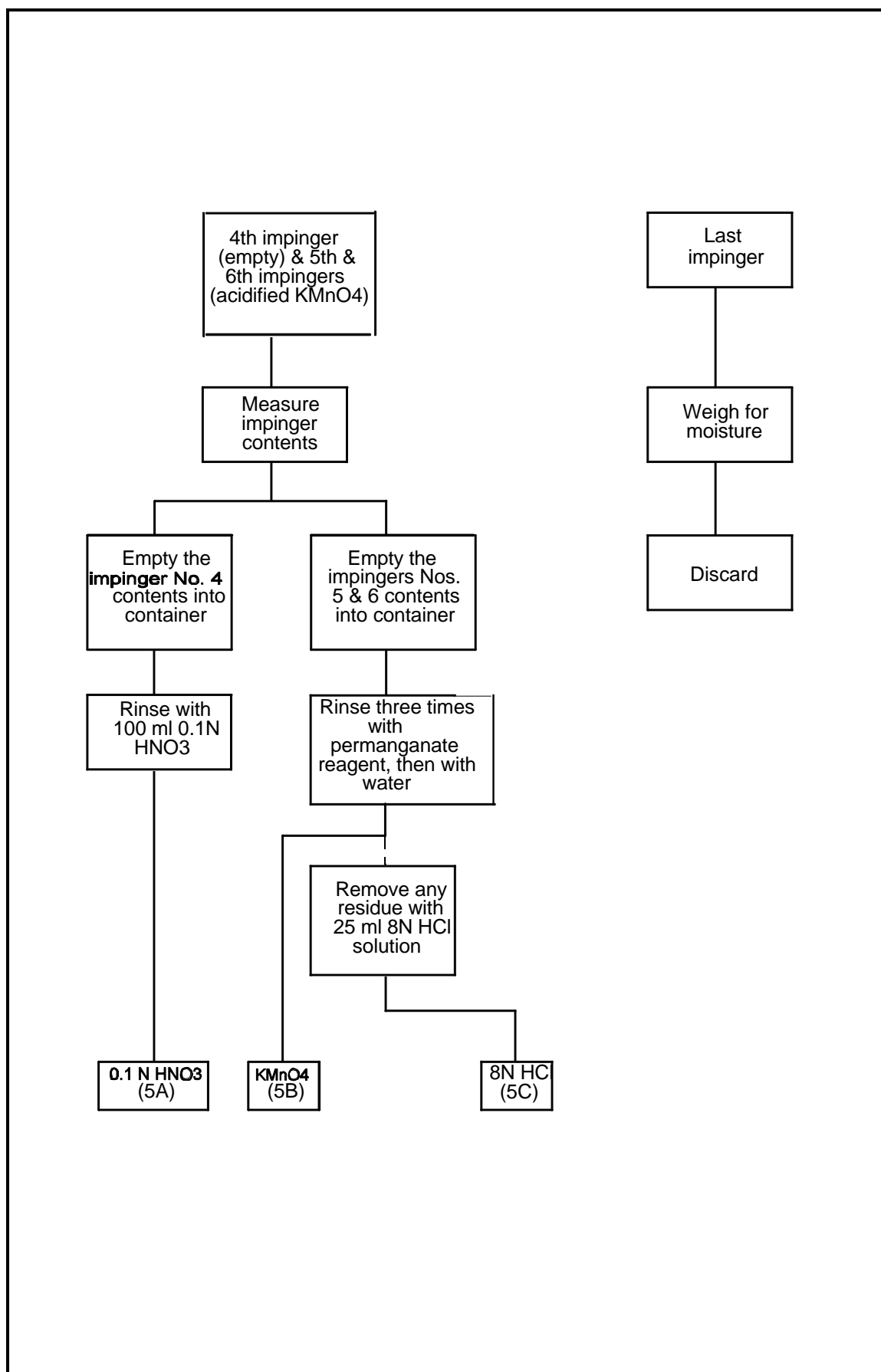


Figure 29-2b. Sample Recovery Scheme.

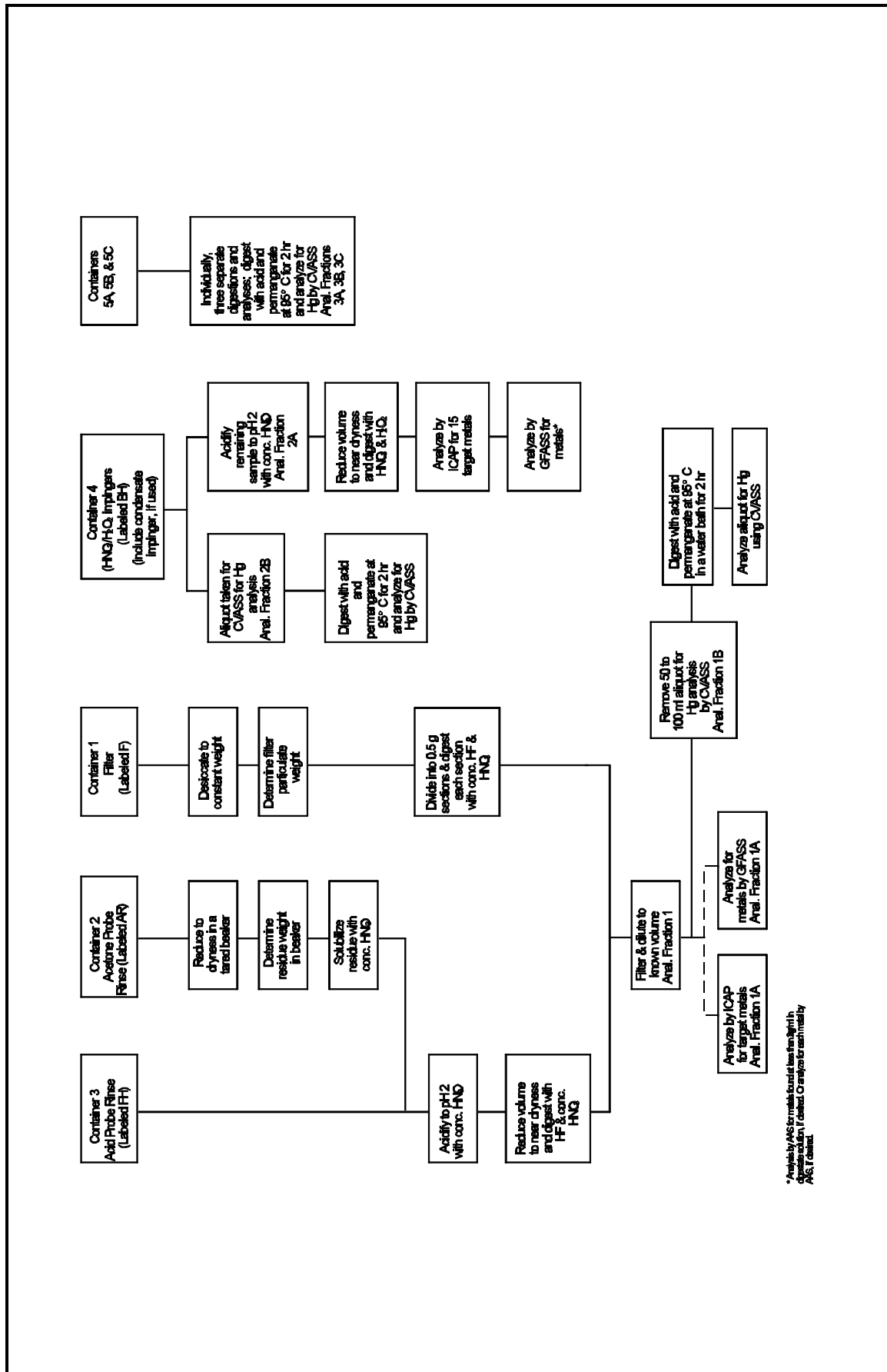


Figure 29-3. Sample Preparation and Analysis Scheme.

**METHOD 3A - DETERMINATION OF OXYGEN AND CARBON DIOXIDE  
CONCENTRATIONS IN EMISSIONS FROM STATIONARY SOURCES  
(INSTRUMENTAL ANALYZER PROCEDURE)**

***1.0 Scope and Application***

**What is Method 3A?**

Method 3A is a procedure for measuring oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 3—Gas Analysis for the Determination of Molecular Weight.
- (c) Method 4—Determination of Moisture Content in Stack Gases.
- (d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. **What does this method determine?** This method measures the concentration of oxygen and carbon dioxide.

Analyte	CAS No.	Sensitivity
Oxygen (O <sub>2</sub> )	7782-44-7	Typically <2% of Calibration Span
Carbon dioxide (CO <sub>2</sub> )	124-38-9	Typically <2% of Calibration Span

1.2 Applicability. **When is this method required?** The use of Method 3A may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans and permits, where measurements of O<sub>2</sub> and CO<sub>2</sub> concentrations in stationary source emissions must be made, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 3A.

1.3 Data Quality Objectives. **How good must my collected data be?** Refer to Section 1.3 of Method 7E.

## ***2.0 Summary of Method***

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of O<sub>2</sub> or CO<sub>2</sub>. You must meet the performance requirements of this method to validate your data.

## ***3.0 Definitions***

Refer to Section 3.0 of Method 7E for the applicable definitions.

## ***4.0 Interferences*** [Reserved]

## ***5.0 Safety***

Refer to Section 5.0 of Method 7E.

## ***6.0 Equipment and Supplies***

Figure 7E-1 in Method 7E is a schematic diagram of an acceptable measurement system.

**6.1 What do I need for the measurement system?** The components of the measurement system are described (as applicable) in Sections 6.1 and 6.2 of Method 7E, except that the analyzer described in Section 6.2 of this method must be used instead of the analyzer described in Method 7E. You must follow the noted specifications in Section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the O<sub>2</sub> or CO<sub>2</sub> concentration on a dry basis, provided that the system is not also being used to concurrently measure SO<sub>2</sub> and/or NO<sub>x</sub>.

**6.2 What analyzer must I use?** You must use an analyzer that continuously measures O<sub>2</sub> or CO<sub>2</sub> in the gas stream and meets the specifications in Section 13.0.

## ***7.0 Reagents and Standards***

**7.1 Calibration Gas. What calibration gases do I need?** Refer to Section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

- (a) CO<sub>2</sub> in nitrogen (N<sub>2</sub>).
- (b) CO<sub>2</sub> in air.
- (c) CO<sub>2</sub>/SO<sub>2</sub> gas mixture in N<sub>2</sub>.
- (d) O<sub>2</sub>/SO<sub>2</sub> gas mixture in N<sub>2</sub>.
- (e) O<sub>2</sub>/CO<sub>2</sub>/SO<sub>2</sub> gas mixture in N<sub>2</sub>.
- (f) CO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>

(g) CO<sub>2</sub>/SO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>

The tests for analyzer calibration error and system bias require high-, mid-, and low-level gases.

#### 7.2 Interference Check. **What reagents do I need for the interference check?**

Potential interferences may vary among available analyzers. Table 7E-3 of Method 7E lists a number of gases that should be considered in conducting the interference test.

### **8.0 Sample Collection, Preservation, Storage, and Transport**

8.1 Sampling Site and Sampling Points. You must follow the procedures of Section 8.1 of Method 7E to determine the appropriate sampling points, unless you are using Method 3A only to determine the stack gas molecular weight and for no other purpose. In that case, you may use single-point integrated sampling as described in Section 8.2 of Method 3. If the stratification test provisions in Section 8.1.2 of Method 7E are used to reduce the number of required sampling points, the alternative acceptance criterion for 3-point sampling will be  $\pm 0.5$  percent CO<sub>2</sub> or O<sub>2</sub>, and the alternative acceptance criterion for single-point sampling will be  $\pm 0.3$  percent CO<sub>2</sub> or O<sub>2</sub>.

8.2 Initial Measurement System Performance Tests. You must follow the procedures in Section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in Section 8.3 of Method 7E apply.

8.3 Interference Check. The O<sub>2</sub> or CO<sub>2</sub> analyzer must be documented to show that interference effects do not exceed 2.5 percent of the calibration span. The interference test in Section 8.2.7 of Method 7E is a procedure that may be used to show this. The effects of all potential interferences at the concentrations encountered during

testing must be addressed and documented. This testing and documentation may be done by the instrument manufacturer.

8.4 Sample Collection. You must follow the procedures in Section 8.4 of Method 7E.

8.5 Post-Run System Bias Check and Drift Assessment. You must follow the procedures in Sections 8.5 of Method 7E.

### ***9.0 Quality Control***

Follow quality control procedures in Section 9.0 of Method 7E.

### ***10.0 Calibration and Standardization***

Follow the procedures for calibration and standardization in Section 10.0 of Method 7E.

### ***11.0 Analytical Procedures***

Because sample collection and analysis are performed together (see Section 8), additional discussion of the analytical procedure is not necessary.

### ***12.0 Calculations and Data Analysis***

You must follow the applicable procedures for calculations and data analysis in Section 12.0 of Method 7E, substituting percent O<sub>2</sub> and percent CO<sub>2</sub> for ppmv of NO<sub>x</sub> as appropriate.

### ***13.0 Method Performance***

The specifications for the applicable performance checks are the same as in Section 13.0 of Method 7E except for the alternative specifications for system bias, drift, and calibration error. In these alternative specifications, replace the term “0.5 ppmv” with the term “0.5 percent O<sub>2</sub>” or “0.5 percent CO<sub>2</sub>” (as applicable).

***14.0 Pollution Prevention*** [Reserved]

***15.0 Waste Management*** [Reserved]

***16.0 Alternative Procedures*** [Reserved]

***17.0 References***

- A. “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards” September 1997 as amended, EPA-600/R-97/121

***18.0 Tables, Diagrams, Flowcharts, and Validation Data***

Refer to Section 18.0 of Method 7E.

**METHOD 6C - DETERMINATION OF SULFUR DIOXIDE EMISSIONS  
FROM STATIONARY SOURCES  
(INSTRUMENTAL ANALYZER PROCEDURE)**

***1.0 Scope and Application***

**What is Method 6C?**

Method 6C is a procedure for measuring sulfur dioxide (SO<sub>2</sub>) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.
- (c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.
- (d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. **What does this method determine?** This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO <sub>2</sub>	7446-09-5	Typically <2% of Calibration Span

1.2 Applicability. **When is this method required?** The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO<sub>2</sub> concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

1.3 Data Quality Objectives. **How good must my collected data be?** Refer to Section 1.3 of Method 7E.

## ***2.0 Summary of Method***

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO<sub>2</sub>. You must meet the performance requirements of this method to validate your data.

## ***3.0 Definitions***

Refer to Section 3.0 of Method 7E for the applicable definitions.

## ***4.0 Interferences***

Refer to Section 4.1 of Method 6.

## ***5.0 Safety***

Refer to Section 5.0 of Method 7E.

## ***6.0 Equipment and Supplies***

Figure 7E-1 of Method 7E is a schematic diagram of an acceptable measurement system.

**6.1 What do I need for the measurement system?** The essential components of the measurement system are the same as those in Sections 6.1 and 6.2 of Method 7E, except that the SO<sub>2</sub> analyzer described in Section 6.2 of this method must be used instead of the analyzer described in Section 6.2 of Method 7E. You must follow the noted specifications in Section 6.1 of Method 7E.

**6.2 What analyzer must I use?** You may use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO<sub>2</sub> in the gas stream and meets the performance specifications in Section 13.0. The low-range and dual-range analyzer provisions in Section 6.2.8.1 of Method 7E apply.

## ***7.0 Reagents and Standards***

**7.1 Calibration Gas. What calibration gases do I need?** Refer to Section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

- (a) SO<sub>2</sub> in nitrogen (N<sub>2</sub>).
- (b) SO<sub>2</sub> in air.
- (c) SO<sub>2</sub> and CO<sub>2</sub> in N<sub>2</sub>.
- (d) SO<sub>2</sub> and O<sub>2</sub> in N<sub>2</sub>.
- (e) SO<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> gas mixture in N<sub>2</sub>.
- (f) CO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>.

(g) CO<sub>2</sub>/SO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>

**7.2 Interference Check. What additional reagents do I need for the interference check?** The test gases for the interference check are listed in Table 7E-3 of Method 7E. For the alternative interference check, you must use the reagents described in Section 7.0 of Method 6.

## **8.0 Sample Collection, Preservation, Storage, and Transport**

**8.1 Sampling Site and Sampling Points.** You must follow the procedures of Section 8.1 of Method 7E.

**8.2 Initial Measurement System Performance Tests.** You must follow the procedures in Section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in Section 8.3 of Method 7E also apply.

**8.3 Interference Check.** You must follow the procedures of Section 8.2.7 of Method 7E to conduct an interference check, substituting SO<sub>2</sub> for NO<sub>x</sub> as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in Section 16 and a co-located, unmodified Method 6 sampling train.

**8.4 Sample Collection.** You must follow the procedures of Section 8.4 of Method 7E.

**8.5 Post-Run System Bias Check and Drift Assessment.** You must follow the procedures of Section 8.5 of Method 7E.

## **9.0 Quality Control**

Follow quality control procedures in Section 9.0 of Method 7E.

### ***10.0 Calibration and Standardization***

Follow the procedures for calibration and standardization in Section 10.0 of Method 7E.

### ***11.0 Analytical Procedures***

Because sample collection and analysis are performed together (see Section 8), additional discussion of the analytical procedure is not necessary.

### ***12.0 Calculations and Data Analysis***

You must follow the applicable procedures for calculations and data analysis in Section 12.0 of Method 7E as applicable, substituting SO<sub>2</sub> for NO<sub>x</sub> as appropriate.

### ***13.0 Method Performance***

13.1 The specifications for the applicable performance checks are the same as in Section 13.0 of Method 7E.

13.2 Alternative Interference Check. When using this procedure, you must document its successful completion for each source category that you test. The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

### ***14.0 Pollution Prevention*** [Reserved]

### ***15.0 Waste Management*** [Reserved]

### ***16.0 Alternative Procedures***

16.1 Alternative Interference Check. You may perform an alternative interference check consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations ( $< 15$  ppm), this alternative interference check is not allowed. **Note:** The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

Build the modified Method 6 sampling train (flow control valve, two midget impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C-1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute ( $\pm 10$  percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midget impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

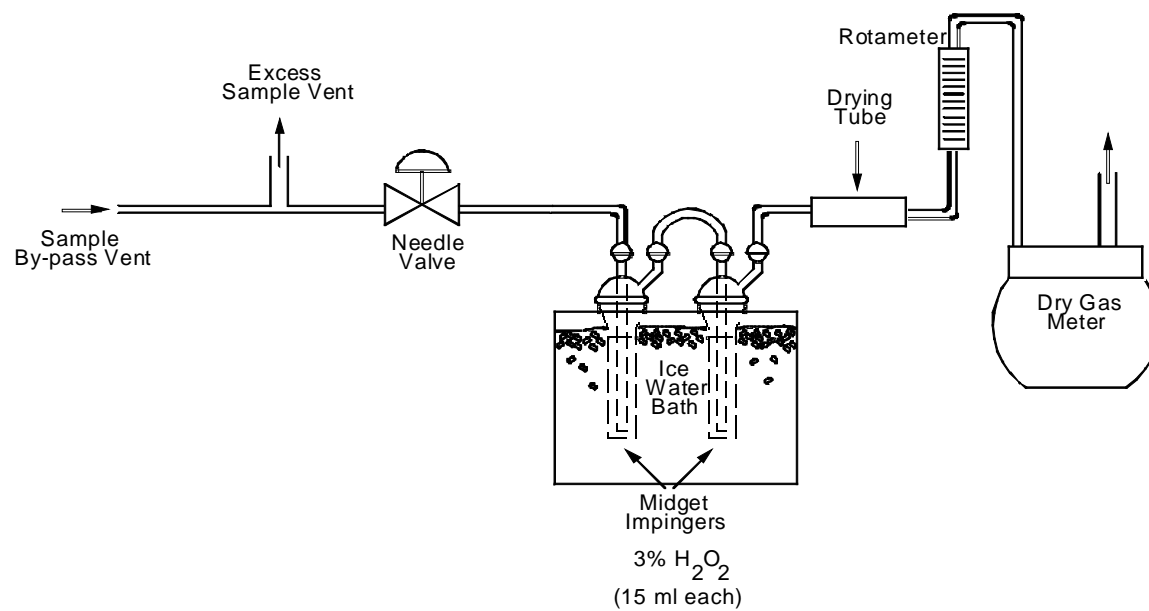
After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers using

the procedures in Method 6. You must analyze performance audit samples as described in Method 6 with this interference check. Determine the average gas concentration reported by Method 6C for the run.

### ***17.0 References***

1. "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997 as amended, EPA-600/R-97/121

### ***18.0 Tables, Diagrams, Flowcharts, and Validation Data***



**Figure 6C-1. Modified Method 6  
Alternative Interference Check Sampling Train**

\* \* \* \* \*

**METHOD 7E - DETERMINATION OF NITROGEN OXIDES EMISSIONS**  
**FROM STATIONARY SOURCES**  
**(INSTRUMENTAL ANALYZER PROCEDURE)**

***1.0 Scope and Application***

**What is Method 7E?**

Method 7E is a procedure for measuring nitrogen oxides (NO<sub>x</sub>) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. **What does this method determine?** This method measures the concentration of nitrogen oxides as NO<sub>2</sub>.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO)	10102-43-9	Typically <2% of Calibration Span
Nitrogen dioxide (NO <sub>2</sub> )	10102-44-0	

1.2 Applicability. **When is this method required?** The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where measurement of NO<sub>x</sub> concentrations in stationary source emissions is required, either to determine compliance with an applicable emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

1.3 Data Quality Objectives (DQO). **How good must my collected data be?** Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

1.4 Data Quality Assessment for Low Emitters. **Is performance relief granted when testing low-emission units?** Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in Section 16 may provide performance relief for certain low-emitting units.

## ***2.0 Summary of Method***

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO<sub>x</sub>. You may measure NO and NO<sub>2</sub> separately or simultaneously together but, for the purposes of this method, NO<sub>x</sub> is the sum of NO and NO<sub>2</sub>. You must meet the performance requirements of this method to validate your data.

## ***3.0 Definitions***

3.1 *Analyzer Calibration Error*, for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

3.2 *Calibration Curve* means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.3 *Calibration Gas* means the gas mixture containing NO<sub>x</sub> at a known concentration and produced and certified in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," September 1997, as amended August 25, 1999, EPA-600/R-97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol.

3.3.1 *Low-Level Gas* means a calibration gas with a concentration that is less than 20 percent of the calibration span and may be a zero gas.

3.3.2 *Mid-Level Gas* means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.3.3 *High-Level Gas* means a calibration gas with a concentration that is equal to the calibration span.

3.4 *Calibration Span* means the upper limit of valid instrument response during sampling. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span

3.5 *Centroidal Area* means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

3.6 *Converter Efficiency Gas* means a calibration gas with a known NO or NO<sub>2</sub> concentration and of Traceability Protocol quality.

3.7 *Data Recorder* means the equipment that permanently records the concentrations reported by the analyzer.

3.8 *Direct Calibration Mode* means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

3.9 *Drift* means the difference between the measurement system readings obtained in the pre-run and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (i.e. low-, mid-, or high-).

3.10 *Gas Analyzer* means the equipment that senses the gas being measured and generates an output proportional to its concentration.

3.11 *Interference Check* means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

3.12 *Low-Concentration Analyzer* means any analyzer that operates with a calibration span of 20 ppm NO<sub>x</sub> or lower. Each analyzer model used routinely to measure low NO<sub>x</sub> concentrations must pass a Manufacturer's Stability Test (MST). A MST subjects the analyzer to a range of potential effects to demonstrate its stability following the procedures provided in 40 CFR 53.23, 53.55, and 53.56 and provides the information in a summary format. A copy of this information must be included in each test report. Table 7E-5 lists the criteria to be met.

3.13 *Measurement System* means all of the equipment used to determine the NO<sub>x</sub> concentration. The measurement system comprises six major subsystems: sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

3.14 *Response Time* means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

3.15 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 *System Bias* means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured, rather than system bias.

3.17 *System Calibration Error* applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

3.18 *System Calibration Mode* means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

3.19 *Test* refers to the series of runs required by the applicable regulation.

#### **4.0 Interferences**

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

#### **5.0 Safety**

**What safety measures should I consider when using this method?** This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas

analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO<sub>2</sub> are toxic and dangerous gases. Nitric oxide is immediately converted to NO<sub>2</sub> upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

## ***6.0 Equipment and Supplies***

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

**6.1 What do I need for the measurement system?** You may use any equipment and supplies meeting the following specifications.

- 1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.
- 2) The interference, calibration error, and system bias criteria must be met.
- 3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.
- 4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point.

Section 6.2 provides example equipment specifications for a NO<sub>x</sub> measurement system. Figure 7E-1 is a diagram of an example dry basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

## 6.2 Measurement System Components

6.2.1 Sample Probe. Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

6.2.2 Particulate Filter. An in-stack or out-of-stack filter. The filter media must be included in the system bias test and made of material that is non-reactive to the gas being sampled. This particulate filter requirement may be waived in applications where no significant particulate matter is expected (e.g., for emission testing of a combustion turbine firing natural gas).

6.2.3 Sample Line. The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E-1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. For systems similar to the one shown in Figure 7E-1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.2.6 Calibration Gas Manifold. Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to block the sample gas flow and flood the sampling probe. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to

transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

**6.2.7 Sample Gas Manifold.** For the type of system shown in Figure 7E-1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

**6.2.8 NO<sub>x</sub> Analyzer.** An instrument that continuously measures NO<sub>x</sub> in the gas stream and meets the applicable specifications in Section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO<sub>2</sub> to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in Section 13.0 are met.

**6.2.8.1 Dual Range Analyzers.** For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that

when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

6.2.8.2 Low Concentration Analyzer. When the calibration span is less than or equal to 20 ppmv, the manufacturer's stability test (MST) is required. See Table 7E-5.

6.2.9 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

## ***7.0 Reagents and Standards***

7.1 Calibration Gas. **What calibration gases do I need?** Your calibration gas must be NO in nitrogen and certified (or recertified) within an uncertainty of 2.0 percent in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997, as amended August 25, 1999, EPA-600/R-97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. The calibration gas must not be used after its expiration date.

Except for applications under part 75 of this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations.

The following calibration gas concentrations are required:

7.1.1 *High-Level Gas*. This concentration sets the calibration span and results in measurements being 20 to 100 percent of the calibration span.

7.1.2 *Mid-Level Gas*. 40 to 60 percent of the calibration span.

7.1.3 *Low-Level Gas*. Less than 20 percent of the calibration span.

7.1.4 *Converter Efficiency Gas*. **What reagents do I need for the converter efficiency test?** The converter efficiency gas for the test described in Section 8.2.4.1 must have a concentration of NO<sub>2</sub> that is between 40 and 60 ppmv. For the alternative converter efficiency tests in Section 16.2, NO is required. In either case, the test gas must be prepared according to the EPA Traceability Protocol.

7.2 Interference Check. **What reagents do I need for the interference check?** Use the appropriate test gases listed in Table 7E-3 (i.e., the potential interferents for the test facility source category, as identified by the instrument manufacturer) to conduct the interference check.

## **8.0 Sample Collection, Preservation, Storage, and Transport**

### **Emission Test Procedure**

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

#### **8.1 What sampling site and sampling points do I select?**

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission

standard, conduct a stratification test as described in Section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

8.1.2 Determination of Stratification. To test for stratification, use a probe of appropriate length to measure the  $\text{NO}_x$  (or pollutant of interest) concentration at twelve traverse points located according to Table 1-1 or Table 1-2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see Section 8.2.6) at each traverse point. Calculate the individual point and mean  $\text{NO}_x$  concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)  $\pm 5.0$  percent of the mean concentration; or (b)  $\pm 0.5$  ppm (whichever is less restrictive), the gas stream is considered unstratified and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)  $\pm 10.0$  percent of the mean; or (b)  $\pm 1.0$  ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified, and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a twelve point stratification test was performed and the emissions shown to be minimally stratified (all points within  $\pm 10.0$  percent of their mean

or within  $\pm 1.0$  ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test, at 0.4, 1.0 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate twelve traverse points for the test in accordance with Table 1-1 or Table 1-2 of Method 1.

8.2 Initial Measurement System Performance Tests. **What initial performance criteria must my system meet before I begin collecting samples?** Before measuring emissions, perform the following procedures:

- (a) Calibration gas verification,
- (b) Measurement system preparation,
- (c) Calibration error test,
- (d) NO<sub>2</sub> to NO conversion efficiency test, if applicable,
- (e) System bias check,
- (f) System response time test, and
- (g) Interference check

8.2.1 Calibration Gas Verification. **How must I verify the concentrations of my calibration gases?** Obtain a certificate from the gas manufacturer and confirm that the documentation includes all information required by the Traceability Protocol. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gases certifications have not expired. This documentation should be available on-site for

inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

**8.2.2 Measurement System Preparation. How do I prepare my measurement system?** Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

**8.2.3 Calibration Error Test. How do I confirm my analyzer calibration is correct?** After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

Record the analyzer's response to each calibration gas on a form similar to Table 7E-1. For each calibration gas, calculate the analyzer calibration error using Equation 7E-1 in Section 12.2 or the system calibration error using Equation 7E-3 in Section 12.4 (as

applicable). The calibration error specification in Section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.4 NO<sub>2</sub> to NO Conversion Efficiency Test . Before each field test, you must conduct an NO<sub>2</sub> to NO conversion efficiency test if your system converts NO<sub>2</sub> to NO before analyzing for NO<sub>x</sub>. Follow the procedures in Section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO<sub>2</sub> fraction in the measured test gas is known. Use Equation 7E-8 in Section 12.8 for this correction.

8.2.4.1 Introduce a concentration of 40 to 60 ppmv NO<sub>2</sub> to the analyzer in direct calibration mode and record the NO<sub>x</sub> concentration displayed by the analyzer. If a dilution-system is used, introduce the NO<sub>2</sub> calibration gas at a point before the dilution takes place. Calculate the converter efficiency using Equation 7E-7 in Section 12.7. The specification for converter efficiency in Section 13.5 must be met. The user is cautioned that state-of-the-art NO<sub>2</sub> calibration gases may not be sufficiently stable and thus make it more difficult to pass the 90 percent conversion efficiency requirement. The NO<sub>2</sub> must be prepared according to the EPA Traceability Protocol and have an accuracy within 2.0 percent.

8.2.4.2 Alternatively, either of the procedures for determining conversion efficiency using NO in Section 16.2 may be used.

8.2.5 Initial System Bias and System Calibration Error Checks. Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of

all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is within 95 percent or 0.5 ppm (whichever is less restrictive) of the certified gas concentration. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E-2.

Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E-2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

From these data, calculate the measurement system response time (see Section 8.2.6) and then calculate the initial system bias using Equation 7E-2 in Section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using equation 7E-3 in Section 12.4. See Section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from Section 8.2.3 and the initial system bias (or 2-point system

calibration error) check until acceptable results are achieved, after which you may begin sampling. (**Note:** For dilution-type systems, data from the 3-point system calibration error test described in Section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

**8.2.6 Measurement System Response Time.** As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

**8.2.7 Interference Check.** Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or similar check on the same make and model of analyzer that you use and provides you with documented results.

You may introduce the appropriate interference test gases (that are potentially encountered during a test, see examples in Table 7E-3) into the analyzer (or measurement system for dilution-type systems) separately or as mixtures. This test must be performed both with and without NO<sub>x</sub> (NO and NO<sub>2</sub>) (the applicable pollutant gas). For analyzers measuring NO<sub>x</sub> greater than 20 ppm, use a calibration gas with an NO<sub>x</sub> concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers

measuring less than 20 ppm NO<sub>x</sub>, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E-4. The specification in Section 13.4 must be met.

A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and included with each test report. This interference test is valid for the life of the instrument unless major analytical components (e.g., the detector) are replaced. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

8.4 Sample Collection. Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points and sample at each point for an equal length of time, maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run. The minimum time you must sample at each point is two times the system response time. Usually the test is designed for sampling longer than this to better characterize the source's temporal variation.

After recording data for the appropriate period of time at the first traverse point, you may move to the next point and continue recording, omitting the requirement to wait for two times the system response time before recording data at the subsequent traverse points. For example, if you use a sampling system with a two-minute system response time, initially purge the system for at least four minutes, then record a minimum of four one-minute averages at each sample point. However, if you remove the probe from the stack, you must recondition the sampling system for at least two times the system response time prior to your next recording.

If at any time a measured one-minute average gas concentration exceeds the calibration span value, you must at a minimum identify and report this as a deviation from the method. Depending on the data quality objectives of the test, this event may require corrective action before proceeding. If the average of any run exceeds the calibration span value, the run is invalidated.

You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a

flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

8.5 Post-Run System Bias Check and Drift Assessment. **How do I confirm that each sample I collect is valid?** After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa.

If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another initial 3-point calibration error test (see Section 8.2.3) and another system bias (or 2-point system calibration error) check (see Section 8.2.5) before repeating the run. In these additional bias and calibration error tests, the gases may be injected in any order. Record the system bias (or system calibration error) check results on a form similar to Table 7E-2.

After each run, calculate the low-level and upscale drift, using Equation 7E-4 in Section 12.5 . If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low- or upscale drift exceeds the specification in Section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

#### 8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure).

**If I want to use the dynamic spike procedure to validate my data, what procedure should I follow?** Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in Section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

8.7 Moisture correction. You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) the applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO<sub>x</sub> analyzer is different from the moisture basis of the Method 3A diluent gas (CO<sub>2</sub> or O<sub>2</sub>) analyzer.

### ***9.0 Quality Control***

**What quality control measures must I take?**

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

Summary Table of QA/QC

Status	Process or Element	QA/QC Specification	Acceptance Criteria	Checking Frequency
S	Identify Data User		Regulatory Agency or other primary end user of data	Before designing test
S	Analyzer Design	Analyzer resolution or sensitivity	$< 2.0\%$ of full-scale range	Manufacturer design
M		Interference gas check	Sum of responses $\leq 2.5\%$ of calibration span Alternatively, sum of responses: $\leq 0.5$ ppmv for calibration spans of 5 to 10 ppmv $\leq 0.2$ ppmv for calibration spans $< 5$ ppmv See Table 7E-3	
M	Calibration Gases	Traceability protocol (G1, G2)	Valid certificate required Uncertainty $\leq 2.0\%$ of tag value	
M		High-level gas	Equal to the calibration span	Each test
M		Mid-level gas	40 to 60% of calibration span	Each test
M		Low-level gas	$< 20\%$ of calibration span	Each test
S	Data Recorder Design	Data resolution	$\leq 0.5\%$ of full-scale range	Manufacturer design
S	Sample Extraction	Probe material	SS or quartz if stack $> 500^{\circ}\text{F}$	Each test

M	Sample Extraction	Probe, filter and sample line temperature	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning  For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	Each run
S	Sample Extraction	Calibration valve material	SS	Each test
S	Sample Extraction	Sample pump material	Inert to sample constituents	Each test
S	Sample Extraction	Manifolding material	Inert to sample constituents	Each test
S	Moisture Removal	Equipment efficiency	< 5% target compound removal	Verified through system bias check
S	Particulate Removal	Filter inertness	Pass system bias check	Each bias check
M	Analyzer & Calibration Gas Performance	Analyzer calibration error (or 3-point system calibration error for dilution systems)	Within $\pm 2.0$ percent of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases Alternative specification: $\leq 0.5$ ppmv absolute difference	Before initial run and after a failed system bias test or drift test
M	System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution Systems)	Within $\pm 5.0$ % of the analyzer calibration span for low-scale and upscale calibration gases Alternative specification: $\leq 0.5$ ppmv absolute difference	Before and after each run

M	System Performance	System response time	Determines minimum sampling time per point	During initial sampling system bias test
M	System Performance	Drift	$\leq 3.0\%$ of calibration span for low-level and mid- or high-level gases  Alternative specification: $\leq 0.5$ ppmv absolute difference	After each test run
M	System Performance	NO <sub>2</sub> -NO conversion efficiency	$\geq 90\%$ of certified test gas concentration	Before each test
M	System Performance	Purge time	$\geq 2$ times system response time	Before starting the first run and when probe is removed from and re-inserted into the stack
M	System Performance	Minimum sample time at each point	Two times the system response time	Each sample point
M	System Performance	Stable sample flow rate (surrogate for maintaining system response time)	Within 10% of flow rate established during system response time check	Each run

M	Sample Point Selection	Stratification test	<p>All points within:  <math>\pm 5\%</math> of mean for 1-point sampling  <math>\pm 10\%</math> of mean for 3-point</p> <p>Alternatively, all points within:  <math>\pm 0.5</math> ppm of mean for 1-point sampling  <math>\pm 1.0</math> ppm of mean for 3-point sampling</p>	Prior to first run
A	Multiple sample points simultaneously	No. of openings in probe	Multi-hole probe with verifiable constant flow through all holes within 10% of mean flow rate (requires Administrative approval for Part 75)	Each run
M	Data Recording	Frequency	$\leq 1$ minute average	During run
S	Data Parameters	Sample concentration range	All 1-minute averages within calibration span	Each run
M	Data Parameters	Average concentration for the run	Run average $\leq$ calibration span	Each run

S = Suggested

M = Mandatory

A = Alternative

## ***10.0 Calibration and Standardization***

### **What measurement system calibrations are required?**

The initial 3-point calibration error test as described in Section 8.2.3 and the system bias (or system calibration error) checks described in Section 8.2.5 are required and must meet the specifications in Section 13 before you start the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias or system calibration error checks described in Section 8.5 are required before and after each run. Your analyzer must be calibrated for all species of NO<sub>x</sub> that it detects. If your analyzer measures NO and NO<sub>2</sub> separately, then you must use both NO and NO<sub>2</sub> calibration gases.

You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

## ***11.0 Analytical Procedures***

Because sample collection and analysis are performed together (see Section 8), additional discussion of the analytical procedure is not necessary.

## ***12.0 Calculations and Data Analysis***

You must follow the procedures for calculations and data analysis listed in this section.

12.1 Nomenclature. **The terms used in the equations are defined as follows:**

ACE	=	Analyzer calibration error, percent of calibration span.
B <sub>WS</sub>	=	Moisture content of sample gas as measured by Method 4 or other approved method, percent/100.
C <sub>Avg</sub>	=	Average unadjusted gas concentration indicated by data recorder for the test run, ppmv
C <sub>D</sub>	=	Pollutant concentration adjusted to dry conditions, ppmv.
C <sub>Dir</sub>	=	Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.
C <sub>Gas</sub>	=	Average effluent gas concentration adjusted for bias, ppmv.
C <sub>M</sub>	=	Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.
C <sub>MA</sub>	=	Actual concentration of the upscale calibration gas, ppmv.
C <sub>O</sub>	=	Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.
C <sub>S</sub>	=	Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.
C <sub>SS</sub>	=	Concentration of NO <sub>x</sub> measured in the spiked sample, ppmv.
C <sub>Spike</sub>	=	Concentration of NO <sub>x</sub> in the undiluted spike gas, ppmv.
C <sub>Calc</sub>	=	Calculated concentration of NO <sub>x</sub> in the spike gas diluted in the sample, ppmv.
C <sub>V</sub>	=	Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv.
C <sub>W</sub>	=	Pollutant concentration measured under moist sample conditions, wet basis, ppmv.
CS	=	Calibration span, ppmv.

- D = Drift assessment, percent of calibration span.
- Eff<sub>NO2</sub> = NO<sub>2</sub> to NO converter efficiency, percent.
- NO<sub>Final</sub> = The average NO concentration observed with the analyzer in the NO mode during the converter efficiency test in Section 16.2.2, ppmv.
- NO<sub>XCorr</sub> = The NO<sub>X</sub> concentration corrected for the converter efficiency, ppmv.
- NO<sub>XFinal</sub> = The final NO<sub>X</sub> concentration observed during the converter efficiency test in Section 16.2.2, ppmv
- NO<sub>XPeak</sub> = The highest NO<sub>X</sub> concentration observed during the converter efficiency test in Section 16.2.2, ppmv
- Q<sub>Spike</sub> = Flow rate of spike gas introduced in system calibration mode, L/min.
- Q<sub>Total</sub> = Total sample flow rate during the spike test, L/min.
- R = Spike recovery, percent.
- SB = System bias, percent of calibration span.
- SB<sub>i</sub> = Pre-run system bias, percent of calibration span.
- SB<sub>f</sub> = Post-run system bias, percent of calibration span.
- SCE = System calibration error, percent of calibration span.
- SCE<sub>i</sub> = Pre-run system calibration error, percent of calibration span.
- SCE<sub>final</sub> = Post-run system calibration error, percent of calibration span.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 7E-1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} \times 100 \quad \text{Eq. 7E-1}$$

12.3 System Bias. For non-dilution systems, use Equation 7E-2 to calculate the system bias separately for the low-level and upscale calibration gases.

$$SB = \frac{C_s - C_{Dir}}{CS} \times 100 \quad \text{Eq. 7E-2}$$

12.4 System Calibration Error. Use Equation 7E-3 to calculate the system calibration error for dilution systems. Equation 7E-3 applies to both the initial 3-point system calibration error test and the subsequent 2-point between run tests.

$$SCE = \frac{C_s - C_v}{CS} \times 100 \quad \text{Eq. 7E-3}$$

12.5 Drift Assessment. Use Equation 7E-4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace “ $SB_{final}$ ” and “ $SB_i$ ” with “ $SCE_{final}$ ” and “ $SCE_i$ ”, respectively, to calculate and evaluate drift.

$$D = |SB_{final} - SB_i| \quad \text{Eq. 7E-4}$$

12.6 Effluent Gas Concentration. For each test run, calculate  $C_{avg}$ , the arithmetic average of all valid  $NO_x$  concentration values (e.g., 1-minute averages). Then adjust the value of  $C_{avg}$  for bias, using Equation 7E-5.

$$C_{Gas} = (C_{Avg} - C_o) \frac{C_{MA}}{C_M - C_o} \quad \text{Eq. 7E-5}$$

12.7  $NO_2$  -  $NO$  Conversion Efficiency. If the  $NO_x$  converter efficiency test described in Section 8.2.4.1 is performed, calculate the efficiency using Equation 7E-7.

$$Eff_{NO2} = \frac{C_{Dir}}{C_v} \times 100 \quad \text{Eq. 7E-7}$$

12.8 NO<sub>2</sub> - NO Conversion Efficiency Correction. If desired, calculate the total NO<sub>x</sub> concentration with a correction for converter efficiency using Equations 7E-8.

$$NO_{xCorr} = NO + \frac{NO_x - NO}{Eff_{NO2}} \times 100 \quad \text{Eq. 7E-8}$$

12.9 Alternative NO<sub>2</sub> Converter Efficiency. If the alternative procedure of Section 16.2.2 is used, calculate the converter efficiency using Equation 7E-9.

$$Eff_{NO2} = \frac{(NO_{xFinal} - NO_{Final})}{(NO_{xPeak} - NO_{xFinal})} \times 100 \quad \text{Eq. 7E-9}$$

12.10 Moisture Correction. Use Equation 7E-10 if your measurements need to be corrected to a dry basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \quad \text{Eq. 7E-10}$$

12.11 Calculated Spike Gas Concentration and Spike Recovery for the Example Alternative Dynamic Spiking Procedure in Section 16.1.3. Use Equation 7E-11 to determine the calculated spike gas concentration. Use Equation 7E-12 to calculate the spike recovery.

$$C_{Calc} = \frac{(C_{Spike})(Q_{Spike})}{Q_{Total}} \quad \text{Eq. 7E-11}$$

$$R = \frac{C_{SS} - C_{Avg}}{C_{Calc}} \times 100 \quad \text{Eq. 7E-12}$$

### 13.0 Method Performance

13.1 Calibration Error. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in Section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must either be within  $\pm 2.0$  percent of the

calibration span. Alternatively, the results are acceptable if  $|C_{dir} - C_v|$  or  $|C_s - C_v|$  (as applicable) is  $\leq 0.5$  ppmv.

13.2 System Bias. This specification is applicable to both the system bias and 2-point system calibration error tests described in Section 8.2.5 and 8.5. The pre- and post-run system bias (or system calibration error) must be within  $\pm 5.0$  percent of the calibration span for the low-level and upscale calibration gases. Alternatively, the results are acceptable if  $|C_s - C_{dir}|$  is  $\leq 0.5$  ppmv or if  $|C_s - C_v|$  is  $\leq 0.5$  ppmv (as applicable).

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.5 ppmv at each gas concentration (i.e.  $|C_{s \text{ post-run}} - C_{s \text{ pre-run}}| \leq 0.5$  ppmv).

13.4 Interference Check. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.50 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span  $< 5$  ppmv.

13.5 NO<sub>2</sub> to NO Conversion Efficiency Test (as applicable). The NO<sub>2</sub> to NO conversion efficiency, calculated according to Equation 7E-7 or Equation 7E-9, must be greater than or equal to 90 percent.

13.6 Alternative Dynamic Spike Procedure. Recoveries of both pre-test spikes and post-test spikes must be within  $100 \pm 10$  percent. If the absolute difference between the calculated

spike value and measured spike value is equal to or less than 0.20 ppmv, then the requirements of the ADSC are met.

**14.0 Pollution Prevention** [Reserved]

**15.0 Waste Management** [Reserved]

**16.0 Alternative Procedures**

16.1 Dynamic Spike Procedure. Except for applications under part 75 of this chapter, you may use a dynamic spiking procedure to validate your test data for a specific test matrix in place of the interference check and pre- and post-run system bias checks. For part 75 applications, use of this procedure is subject to the approval of the Administrator. Best results are obtained for this procedure when source emissions are steady and not varying. Fluctuating emissions may render this alternative procedure difficult to pass. To use this alternative, you must meet the following requirements.

16.1.1 Procedure Documentation. You must detail the procedure you followed in the test report, including how the spike was measured, added, verified during the run, and calculated after the test.

16.1.2 Spiking Procedure Requirements. The spikes must be prepared from EPA Traceability Protocol gases. Your procedure must be designed to spike field samples at two target levels both before and after the test. Your target spike levels should bracket the average sample NO<sub>x</sub> concentrations. The higher target concentration must be less than the calibration span. You must collect at least 5 data points for each target concentration. The spiking procedure must be performed before the first run and repeated after the last run of the test program.

16.1.3 Example Spiking Procedure. Determine the NO concentration needed to generate concentrations that are 50 and 150 percent of the anticipated NO<sub>x</sub> concentration in the stack at the total sampling flow rate while keeping the spike flow rate at or below 10 percent of this total. Use a mass flow meter (accurate within 2.0 percent) to generate these NO spike gas concentrations at a constant flow rate. Use Equation 7E-11 in Section 12.11 to determine the calculated spike concentration in the collected sample.

Prepare the measurement system and conduct the analyzer calibration error test as described in Sections 8.2.2 and 8.2.3. Following the sampling procedures in Section 8.1, determine the stack NO<sub>x</sub> concentration and use this concentration as the average stack concentration ( $C_{avg}$ ) for the first spike level, or if desired, for both pre-test spike levels. Introduce the first level spike gas into the system in system calibration mode and begin sample collection. Wait for at least two times the system response time before measuring the spiked sample concentration. Then record at least five successive 1-minute averages of the spiked sample gas. Monitor the spike gas flow rate and maintain at the determined addition rate. Average the five 1-minute averages and determine the spike recovery using Equation 7E-12. Repeat this procedure for the other pre-test spike level. The recovery at each level must be within the limits in Section 13.6 before proceeding with the test.

Conduct the number of runs required for the test. Then repeat the above procedure for the post-test spike evaluation. The last run of the test may serve as the average stack concentration for the post-test spike test calculations. The results of the post-test spikes must meet the limits in Section 13.6.

16.2 Alternative NO<sub>2</sub> to NO Conversion Efficiency Procedures. You may use either of the following procedures to determine converter efficiency in place of the procedure in Section 8.2.4.1.

16.2.1 The procedure for determining conversion efficiency using NO in 40 CFR 86.123-78.

16.2.2 Tedlar Bag Procedure. Perform the analyzer calibration error test to document the calibration (both NO and NO<sub>x</sub> modes, as applicable). Fill a Tedlar bag approximately half full with either ambient air, pure oxygen, or an oxygen standard gas with at least 19.5 percent by volume oxygen content. Fill the remainder of the bag with mid-level NO in nitrogen calibration gas. (Note that the concentration of the NO standard should be sufficiently high that the diluted concentration will be easily and accurately measured on the scale used. The size of the bag should be large enough to accommodate the procedure and time required).

Immediately attach the bag to the inlet of the NO<sub>x</sub> analyzer (or external converter if used). In the case of a dilution-system, introduce the gas at a point upstream of the dilution assembly. Measure the NO<sub>x</sub> concentration for a period of 30 minutes. If the NO<sub>x</sub> concentration drops more than 2 percent absolute from the peak value observed, then the NO<sub>2</sub> converter has failed to meet the criteria of this test. Take corrective action. The highest NO<sub>x</sub> value observed is considered to be NO<sub>xPeak</sub>. The final NO<sub>x</sub> value observed is considered to be NO<sub>xfinal</sub>.

If the NO<sub>x</sub> converter has met the criterion of this test, then switch the analyzer to the NO mode (note that this may not be required for analyzers with auto-switching). Document the average NO concentration for a period of 30 seconds to one minute. This average value is

NO<sub>final</sub>. Switch the analyzer back to the NO<sub>x</sub> mode and document that the analyzer still meets the criteria of not dropping more than 2 percent from the peak value.

In sequence, inject the zero and the upscale calibration gas that most closely matches the NO<sub>x</sub> concentration observed during the converter efficiency test. Repeat this procedure in both the NO and NO<sub>x</sub> modes. If the gases are not within 1 percent of scale of the actual values, reject the converter efficiency test and take corrective action. If the gases are within this criterion, use Equation 7E-9 to determine the converter efficiency. The converter efficiency must meet the specification in Section 13.5.

16.3 Manufacturer's Stability Test. A manufacturer's stability test is required for all analyzers that routinely measure emissions below 20 ppm and is optional but recommended for other analyzers. This test evaluates each analyzer model by subjecting it to the tests listed in Table 7E-5 following the procedures in 40 CFR Part 53.23, 53.55, and 53.56 to demonstrate its stability. A copy of this information in summary format must be included in each test report.

## ***17.0 References***

1. "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997 as amended, EPA-600/R-97/121.

## ***18.0 Tables, Diagrams, Flowcharts, and Validation Data***

Figure 7E-1. Measurement System

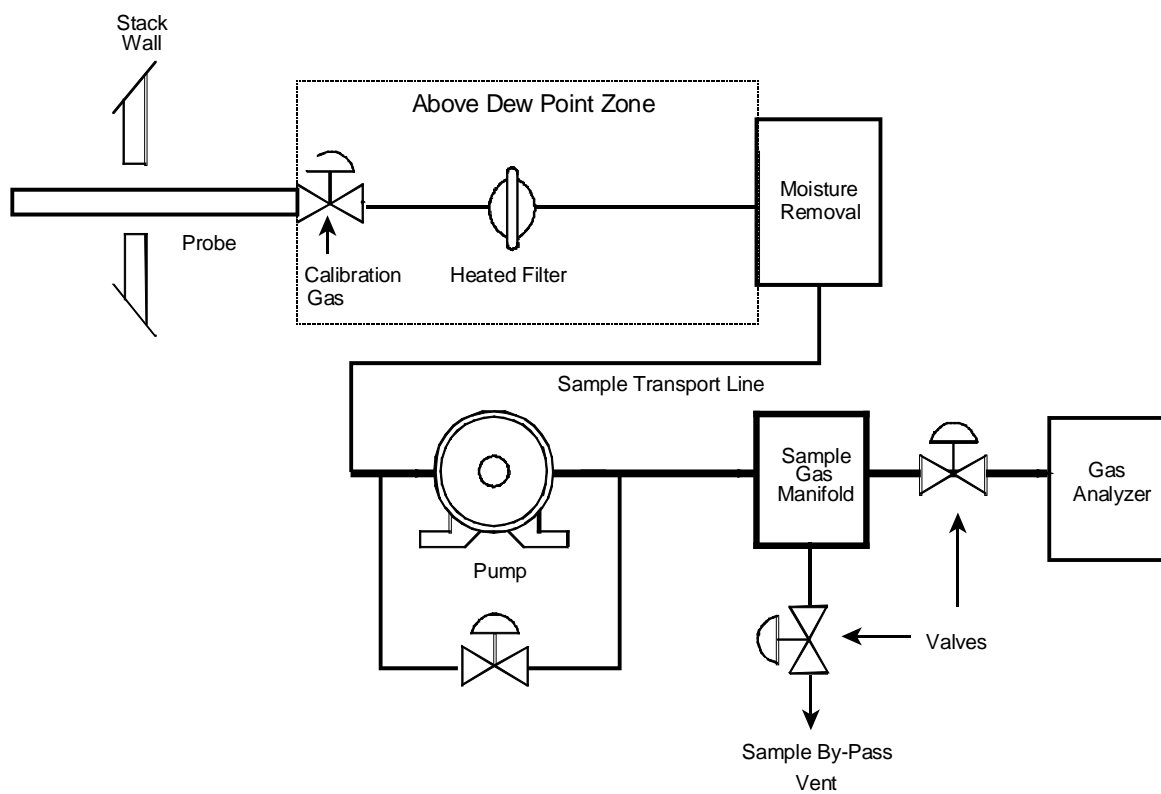
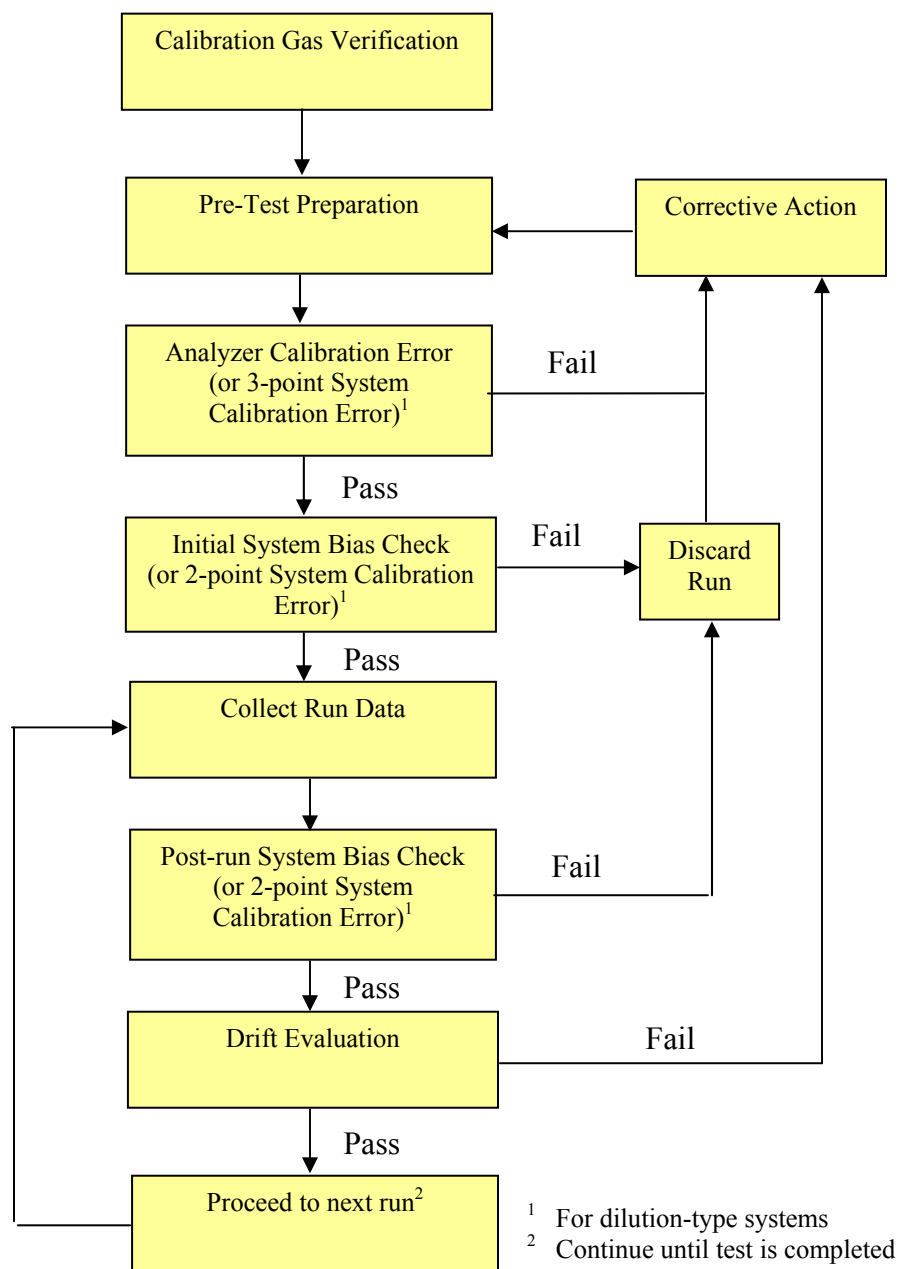


Figure 7E-2. Testing Flow Chart



**Table 7E-1 - Analyzer (or System) Calibration Error Data**

Source Identification: _____		Analyzer <sup>1</sup> or System <sup>2</sup> calibration error data for sampling runs: _____		
Test personnel: _____		Analyzer Model No. _____		
Date: _____		Serial No. _____		
Time: _____		Calibration Span (CS): _____		
	Manufacturer Certified Cylinder Value (indicate units)	Analyzer calibration response (indicate units)	Absolute difference (indicate units)	Calibration Error (percent of calibration span)
	A	B	A-B	$\frac{A-B}{CS} \times 100$
Low-level (or zero) calibration gas	.....	.....	.....	.....
Mid-level calibration gas.....	.....	.....	.....	.....
High-level calibration gas ....	.....	.....	.....	.....

<sup>1</sup> Refers to data from the analyzer calibration error test of a non-dilution system.<sup>2</sup> Refers to data from a 3-point system calibration error test of a dilution system.

**Table 7E-2 - System Bias (or System Calibration Error) and Drift Data**

Source Identification: \_\_\_\_\_ Run Number: \_\_\_\_\_

Test personnel: \_\_\_\_\_ Calibration Span: \_\_\_\_\_

Date: \_\_\_\_\_ Response Time: \_\_\_\_\_

Analyzer Model No. \_\_\_\_\_ Serial No. \_\_\_\_\_

Initial values				Final values		
Calibration Gas Level	Certified Calibration gas value (indicate units)	System Response (indicate units)	System Bias <sup>1</sup> or Calibration Error <sup>2</sup> (% of calibration span)	System response (indicate units)	System Bias <sup>1</sup> or Calibration Error <sup>2</sup> (% of calibration span)	Drift (% of calibration span)
Low-level gas .....	.....	.....	.....	.....	.....	.....
Upscale (high- or mid-) level gas .....	.....	.....	.....	.....	.....	.....

<sup>1</sup> Refers to the pre- and post-run system bias checks of a non-dilution system.<sup>2</sup> Refers to the pre- and post-run system calibration error checks of a dilution system.

**Table 7E-3. Interference Check Gas Concentrations**

<b>Potential Interferent</b>	<b>Sample Conditioning Type<sup>2</sup></b>	
	<b>Hot Wet</b>	<b>Dried</b>
<b>CO<sub>2</sub></b>	<b>5 and 15%</b>	<b>5 and 15%</b>
<b>H<sub>2</sub>O</b>	<b>25%</b>	<b>1 %</b>
<b>NO</b>	<b>15 ppmv</b>	<b>15 ppmv</b>
<b>NO<sub>2</sub></b>	<b>15 ppmv</b>	<b>15 ppmv</b>
<b>N<sub>2</sub>O</b>	<b>10 ppmv</b>	<b>10 ppmv</b>
<b>CO</b>	<b>50 ppmv</b>	<b>50 ppmv</b>
<b>NH<sub>3</sub></b>	<b>10 ppmv</b>	<b>10 ppmv</b>
<b>CH<sub>4</sub></b>	<b>50 ppmv</b>	<b>50 ppmv</b>
<b>SO<sub>2</sub></b>	<b>20 ppmv</b>	<b>20 ppmv</b>
<b>H<sub>2</sub></b>	<b>50 ppmv</b>	<b>50 ppmv</b>
<b>HCl</b>	<b>10 ppmv</b>	<b>10 ppmv</b>

- 1) Any of the above specific gases can be eliminated or tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.
- 2) For dilution extractive systems, use the Hot Wet concentrations divided by the minimum targeted dilution ratio to be used during the test.

**Table 7E-4 - Interference Response**

Date of Test: \_\_\_\_\_

Analyzer Type: \_\_\_\_\_

Model No.: \_\_\_\_\_

Serial No.: \_\_\_\_\_

Calibration Span: \_\_\_\_\_

Test Gas Type	Concentration (ppm)	Analyzer Response
Sum of Responses		
% of Calibration Span		

**Table 7E-5. Manufacturer Stability Test***Each Model Must Be Tested Quarterly or Once Per 50 Production Units*

TEST DESCRIPTION	Acceptance Criteria (Note 1)
Thermal Stability	Temperature range when drift does not exceed 3.0% of analyzer range over a 12-hour run when measured with NO <sub>x</sub> present @ $\geq$ 80% of calibration span.
Fault Conditions	Identify conditions which, when they occur, result in performance which is not in compliance with the Manufacturer's Stability Test criteria. These are to be indicated visually or electrically to alert the operator of the problem.
Insensitivity to Supply Voltage Variations	$\pm 10.0\%$ (or manufacturers alternative) variation from nominal voltage must produce a drift of $\leq 2.0\%$ of calibration span for either zero or concentration $\geq 80\%$ NO <sub>x</sub> present
Analyzer Calibration Error	For a low-, medium-, and high- calibration gas, the difference between the manufacturer certified value and the analyzer response in direct calibration mode, no more than 2.0% of calibration span

Note 1: If the instrument is to be used as a Low Range analyzer, all tests must be performed at a calibration span of 20 ppm or less.

**METHOD 10 - DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM  
STATIONARY SOURCES  
(INSTRUMENTAL ANALYZER PROCEDURE)**

***1.0 Scope and Application***

**What is Method 10?**

Method 10 is a procedure for measuring carbon monoxide (CO) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.
- (c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

1.1 Analytes. **What does this method determine?** This method measures the concentration of carbon monoxide.

Analyte	CAS No.	Sensitivity
CO	630-08-0	Typically <2% of Calibration Span

1.2 Applicability. **When is this method required?** The use of Method 10 may be required by specific New Source Performance Standards, State Implementation Plans, and permits where CO concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 10.

1.3 Data Quality Objectives. Refer to Section 1.3 of Method 7E.

## ***2.0 Summary of Method***

In this method, you continuously or intermittently sample the effluent gas and convey the sample to an analyzer that measures the concentration of CO. You must meet the performance requirements of this method to validate your data.

## ***3.0 Definitions***

Refer to Section 3.0 of Method 7E for the applicable definitions.

## ***4.0 Interferences***

Substances having a strong absorption of infrared energy may interfere to some extent in some analyzers. Instrumental correction may be used to compensate for the interference. You

may also use silica gel and ascarite traps to eliminate the interferences. If this option is used, correct the measured gas volume for the carbon dioxide (CO<sub>2</sub>) removed in the trap.

## **5.0 Safety**

Refer to Section 5.0 of Method 7E.

## **6.0 Equipment and Supplies**

### **What do I need for the measurement system?**

6.1 Continuous Sampling. Figure 7E-1 of Method 7E is a schematic diagram of an acceptable measurement system. The components are the same as those in Sections 6.1 and 6.2 of Method 7E, except that the CO analyzer described in Section 6.2 of this method must be used instead of the analyzer described in Section 6.2 of Method 7E. You must follow the noted specifications in Section 6.1 of Method 7E except that the requirements to use stainless steel, Teflon, or non-reactive glass filters do not apply. Also, a heated sample line is not required to transport dry gases or for systems that measure the CO concentration on a dry basis.

#### 6.2 Integrated Sampling.

6.2.1 Air-Cooled Condenser or Equivalent. To remove any excess moisture.

6.2.2 Valve. Needle valve, or equivalent, to adjust flow rate.

6.2.3 Pump. Leak-free diaphragm type, or equivalent, to transport gas.

6.2.4 Rate Meter. Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per minute (0.035 cfm).

6.2.5 Flexible Bag. Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft<sup>3</sup>).

Leak-test the bag in the laboratory before using by evacuating with a pump followed by a dry gas meter. When the evacuation is complete, there should be no flow through the meter.

**6.3 What analyzer must I use?** You must use an instrument that continuously measures CO in the gas stream and meets the specifications in Section 13.0. The dual-range analyzer provisions in Section 6.2.8.1 of Method 7E apply.

## ***7.0 Reagents and Standards***

**7.1 Calibration Gas. What calibration gases do I need?** Refer to Section 7.1 of Method 7E for the calibration gas requirements.

**7.2 Interference Check. What additional reagents do I need for the interference check?** Use the appropriate test gases listed in Table 7E-3 of Method 7E (i.e., potential interferences, as identified by the instrument manufacturer) to conduct the interference check.

## ***8.0 Sample Collection, Preservation, Storage, and Transport***

### **Emission Test Procedure**

**8.1 Sampling Site and Sampling Points.** You must follow Section 8.1 of Method 7E.

**8.2 Initial Measurement System Performance Tests.** You must follow the procedures in Section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in Section 8.3 of Method 7E also apply.

**8.3 Interference Check.** You must follow the procedures of Section 8.2.7 of Method 7E.

**8.4 Sample Collection.**

**8.4.1 Continuous Sampling.** You must follow the procedures of Section 8.4 of Method 7E.

**8.4.2 Integrated Sampling.** Evacuate the flexible bag. Set up the equipment as shown in Figure 10-1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak-free. Sample at a rate proportional to

the stack velocity. If needed, the CO<sub>2</sub> content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing an ascarite CO<sub>2</sub> removal tube used and computing CO<sub>2</sub> concentration from the gas volume sampled and the weight gain of the tube. Data may be recorded on a form similar to Table 10-1.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures in Sections 8.5 and 8.6 of Method 7E.

### ***9.0 Quality Control***

Follow the quality control procedures in Section 9.0 of Method 7E.

### ***10.0 Calibration and Standardization***

Follow the procedures for calibration and standardization in Section 10.0 of Method 7E.

### ***11.0 Analytical Procedures***

Because sample collection and analysis are performed together (see Section 8), additional discussion of the analytical procedure is not necessary.

### ***12.0 Calculations and Data Analysis***

You must follow the procedures for calculations and data analysis in Section 12.0 of Method 7E, as applicable, substituting CO for NO<sub>x</sub> as applicable.

12.1 Concentration Correction for CO<sub>2</sub> Removal. Correct the CO concentration for CO<sub>2</sub> removal (if applicable) using Eq. 10-1.

$$C_{Avg} = C_{CO\ stack} (1 - F_{CO2})$$

Where:

C<sub>Avg</sub> = Average gas concentration for the test run, ppm.

$C_{\text{CO stack}}$  = Average unadjusted stack gas CO concentration indicated by the data recorder for the test run, ppmv.

$F_{\text{CO}_2}$  = Volume fraction of CO<sub>2</sub> in the sample, i.e., percent CO<sub>2</sub> from Orsat analysis divided by 100.

### ***13.0 Method Performance***

The specifications for analyzer calibration error, system bias, drift, interference check, and alternative dynamic spike procedure are the same as in Section 13.0 of Method 7E.

### ***14.0 Pollution Prevention*** [Reserved]

### ***15.0 Waste Management*** [Reserved]

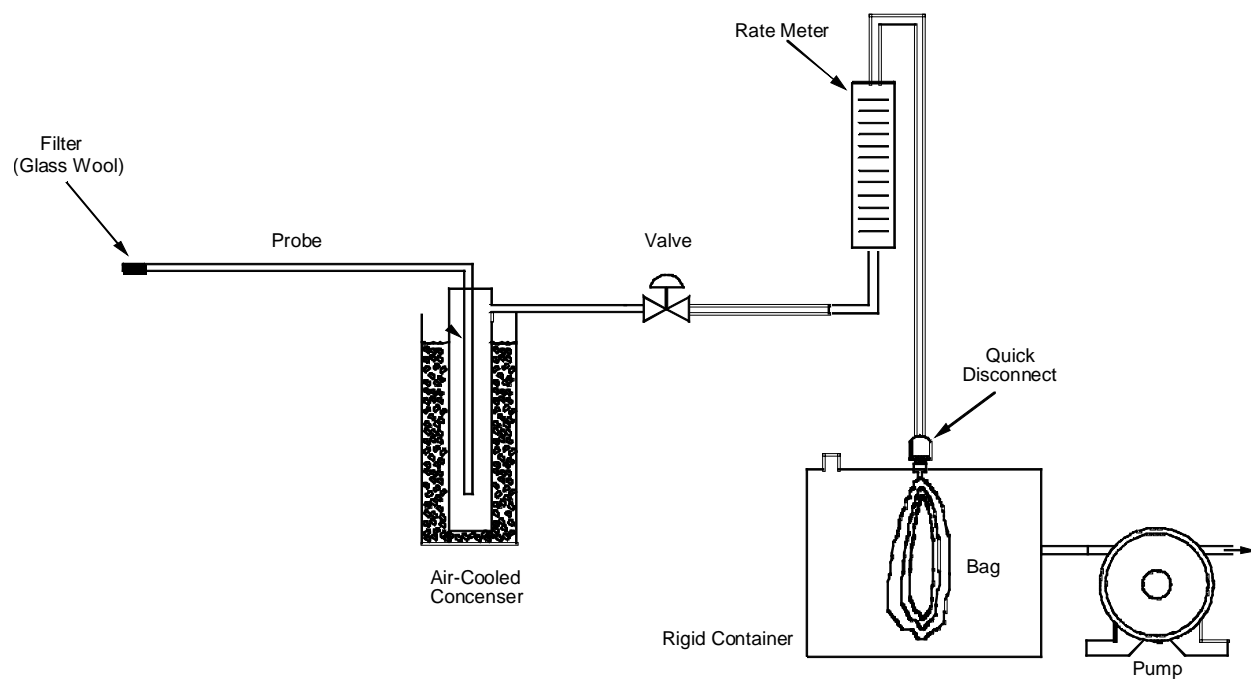
### ***16.0 Alternative Procedures***

The dynamic spike procedure and the manufacturer stability test are the same as in Sections 16.1 and 16.3 of Method 7E

### ***17.0 References***

1. "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997 as amended, EPA-600/R-97/121

### ***18.0 Tables, Diagrams, Flowcharts, and Validation Data***

**Figure 10-1. Integrated Gas Sampling Train.**

**TABLE 10-1 - FIELD DATA**  
**Integrated Sampling**

[illegible]